INVESTIGATION OF OIL ADSORPTION CAPACITY OF GRANULAR ORGANOCLAY MEDIA AND THE KINETICS OF OIL REMOVAL FROM OIL-IN-WATER EMULSIONS

A Thesis

by

SONIA ISLAM

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2006

Major Subject: Civil Engineering

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Approved by:

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	Roy Hann
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ABSTRACT

Investigation of Oil Adsorption Capacity of Granular Organoclay Media and the
Kinetics of Oil Removal from Oil-in-Water Emulsions. (December 2006)

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Co-Chairs of Advisory Committee: Dr. Maria A. Barrufet
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Produced water, a byproduct of oil and gas production, includes almost 98% of all waste generated by oil and gas exploration and their production activities. This oil contaminated waste water has a great impact on our environment and is considered to be a high-cost liability. The Department of Energy’s Oil and Gas Environmental Program is concerned with the development of new and affordable technology to clean this produced water. Organically modified clays are proposed as a good option for removal of oil from produced water. Organoclay, incorporated into a treatment process shows promise of being a cost effective method of treatment to remove crude oil from brine either as a final treatment prior to brine disposal at sea or as a precursor to desalination. Organoclay also pre-polishes the waste water before further treatment. This research studies the efficacy of using organoclay to remove oil by measuring its adsorption capacity to remove the oil from a SAE 30 (Golden West Superior) motor oil-water emulsion. A kinetic model was developed to examine the time dependent behavior of the oil adsorbing characteristics of the organoclay and to investigate how closely the experimentally obtained data matches the kinetic model. It was found that organoclay is effective in removing various percentages of oil depending on the concentrations of a SAE 30 (Golden West Superior) motor oil-water emulsion. Moreover, it was found that the experimental data closely follow the kinetic behavior of the organoclay as shown by the kinetic model. Since this research is specific to a particular type of oil, SAE 30, further research is required for verifying the adsorption capacity of organoclay in other types of oils. Moreover, it is also recommended that the adsorption capacity of the organoclay, together with conventional adsorbent such as GAC (Granular Activated Carbon), be investigated to determine if there is any further improvement in the adsorption capacity. Lastly, a detailed investigation using the actual produced water from the oil field should be conducted to determine the efficacy of the organoclay system in removing oil from water produced in the field.

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CHAPTER I

INTRODUCTION

1.1 Produced water and its impact on the environment

Conventionally, produced water is viewed as a by-product of oil production. Produced water can be defined as complex brine that is usually hot and corrosive and contains undesirable components such as organic chemicals, salts, hydrogen sulfide etc. Sometimes significant amount of heavy metals, aromatic hydrocarbons and radioactive compounds can be found in produced water. A huge variety of produced water exists depending on the nature of the oil field they come from. These variations lead to water being highly variable in quality and unstable and as a result, facilities for handling produced water tend to be relatively complex, especially when treatment is required to remove dissolved hydrocarbons, heavy metals and dispersed oil in addition to the removal of the salts.[1]

A large volume of produced water is generated along with the petroleum resource during the oil and gas production (O&G). In fact the management and disposal of produced water is considered to be one of the most significant problems associated with oil and gas production. The produced water production is generally indicated by a by a term known as water cut. Water cut can be defined as the ratio of water produced

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This thesis follows the style of the *Journal of Petroleum Technology.*

compared to the volume of total liquids produced.[2] Typically, the water cut ratio is around 10:1, sometimes even more. With such a large volume, the disposal of produced water associated with oil and gas production becomes really expensive for the operator and affects both the economics of the reservoir and the environment. Moreover, day by day discharge standards are getting more and more stringent in most of the operating areas of the world. Therefore, produced water treatment and disposal have become subjects of growing attention and interest in exploration and production operations everywhere.

Under the Clean Water Act, the discharge of produced water to the surface and seawater is prohibited until certain criteria are met. If discharge of produced water to the sea is allowed, it will have to meet certain quality standards of a particular area. The U.S. Environmental Protection Agency (EPA) classifies oil production by offshore and coastal regions. BAT (Best Available Technology) effluent limitations specify a maximum of 29 mg/l. oil in the water, averaged over 30 days. Offshore BCT (Best Conventional Technology) regulations specify 48mg/l, averaged over 30 days.[1] In fact, after suitable chemical treatment; it is not difficult to maintain these federal limits in the produced water. But that is not the final scenario as state regulations, on many occasions, tend to be more stringent than the federal regulations.[1] A specific example can be given here to clarify this issue. “Chapter 4 of Wyoming Water Quality Rules and Regulations deals not only with oil from produced water, but also from with water contaminated by fuel oil, gasoline, aviation fuel, etc. Section 4a says oil releases shall not be present in amounts that would cause conditions such as oil and grease content over 10 mg/l.”[1] This example shows that oil release standard in state regulation is more stringent than federal regulation as state regulations does not allow release rate more than 10 mg/l, whereas, the Federal regulations allows a release rate as high as 29 mg/l.

On top of all the issues described above, a high capital and operating cost is also associated with this produced water handling processes which makes the oil and gas production expensive. Therefore, something has to be done to reduce this "high cost" related to the produced water. This cost can be as high as \$1.5/bbl of produced water if the produce water has to be transported to other sites for disposal purpose.[3] Environmental management of produced water can be conducted in several ways. Following are some of the typically followed environmental management methods:[4]

- Reduce
- Re-use
- Recycle/Recover
- Treatment

The preferred method for the disposal of produced water has to be such that it does not produce anything that is toxic for the environment. Cost is also an important selection criterion. Regulatory authorities, public opinion and ethics often curb the options available to the operator. Therefore it can be said that water quality and treatment facility design decisions are critical and must be carefully made on a case-by-case basis. In the next chapter, we will explore some commonly used methods of treating produced water and discuss their working principle.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Present concern for produced water treatment

Salt water that is produced along with the hydrocarbons during oil and gas production is known as produced water in the oil industry. According to the Environmental Protection Agency (EPA) the official definition of the produced water is given as: [5]

"Produced water means the water brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil-water separation process."

As mentioned before, produced water management has been a major headache for the exploration and production (E&P) industry due to its compelling effects on production operations. Because the volume of this produced water is very large and because produced water has the potential to cause detrimental effects on the environment, proper management of this water is a must. More than 4-million barrels of brine (over 150 million gallons) are produced in Texas alone everyday.[6]

Produced water and its effects have been studied intensely by many researchers. Ukpohore *et al.* [7] studied offshore and onshore areas in Nigeria and found with great concern that many E&P companies do not follow effective produced water treatment technologies. Therefore he concluded that, in the near future, the discharge of produced water would become a cause of intense environmental hazards to those specific areas.

Cost is a vital issue for disposal of oil field produced water. Therefore it is always desirable to offset this cost in some fashion. That's why Lawrence *et al.*[8, 9] evaluated various cost effective and environmentally satisfactory methods for disposal of oilfield produced water. According to their study, the properly treated produced water, which maintains the water quality standard, can be used for beneficial purposes such as irrigation or watering live stock.

One other important issue for produced water is its impact on the environment. Georgia *et al.*[10] studied this aspect. They described how environmental challenges had become a major concern in the oil & gas industry with the increased quantity of produced water being dealt with in the North Sea.

Thus, from various studies, it can be seen that produced water has been a concern due to its effect to the environment and the cost associated with its management. Some of the cost can definitely be offset from its reuse. However, proper treatment of produced water is mandatory before one can reuse it. Therefore, it can easily be said that, treatment of produced water is very critical to the oil and gas (O&G) production sector. In pursuit of this treatment of produced water; engineers are conducting research to come up with various techniques that can ensure the most stringent discharge standard of the oil contaminated produced water before discharging it to the environment. The economics of the reservoirs is strongly dependent on the produced water disposal system. Also, due to stringent regulations, exploration and production (E & P) industries are spending money for produced water management and handling system. Therefore, the most desirable method to dispose or treat the produced water will be the one that conserves the environment in an economical way.[11] Engineers have to remember these two criteria while developing a method for produced water treatment. In the next section, some of the current produced water management procedures will be discussed.

2.2 Current produced water management practices

A brief description of the currently followed produced water management practices will be enumerated in this section. These are actually produced water management process, not treating processes.

2.2.1 Downhole separation

The process of separating and allowing the water to flow back to the reservoir without bringing it up to the surface is known as downhole separation process. Downhole separation technology minimizes the quantity of produced water by separating it from the oil downhole and injecting it underground. Many components are included in this system, but the primary one is an oil-water separation system. Typically, two major types of downhole separating systems are currently in use. One type uses hydrocyclones to mechanically separate oil and water, and the other type relies on gravity separation that takes place in the well bore. [12, 13] Fig. 1 schematically shows a downhole separation system.

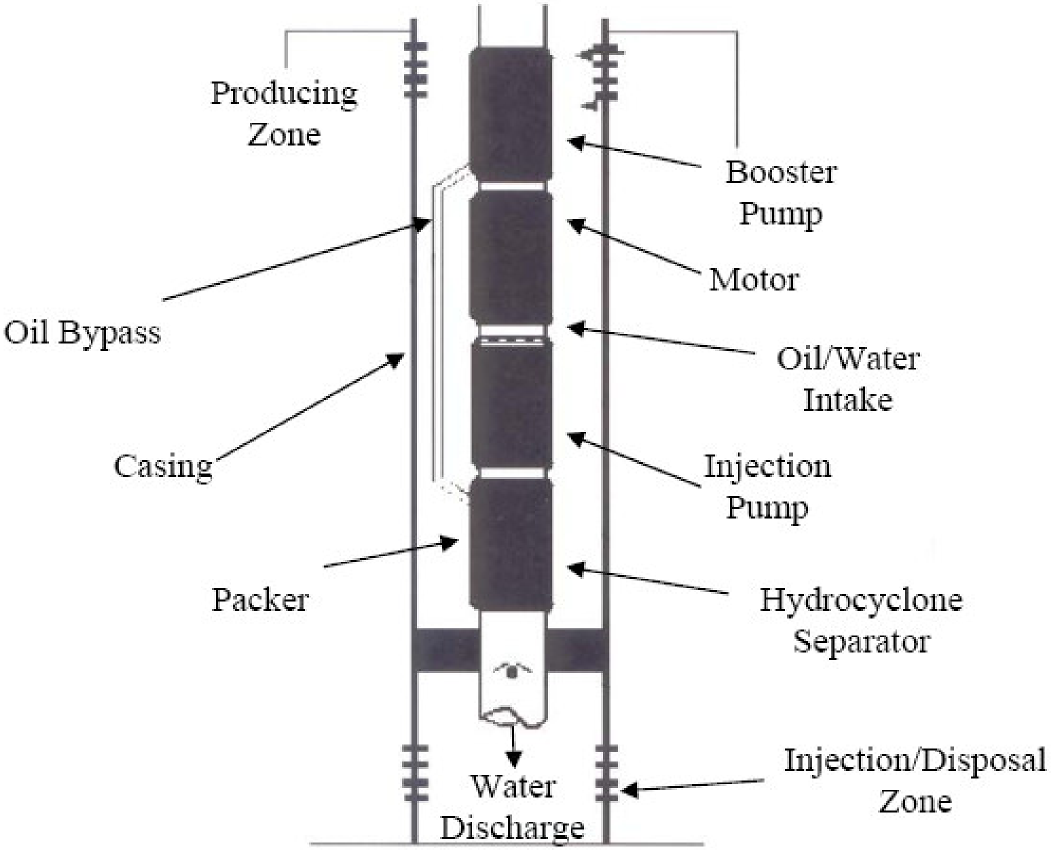


Fig. 1- Schematic diagram of downhole separation system [12]

The Department of Environment (DOE) is actively promoting this downhole separation system. Oil-water separators (DOWS) can be used to enhance the water handling and production rate on a field-wide basis. Gravity separator-type DOWS are intended to permit the oil droplets that enter a well bore through perforations to rise and form an isolated oil layer in the well. Gravity separator tools which are vertically adjusted have two intakes, one in the oil layer and the other in the water layer.[14] This type of DOWS uses rod pumps. As it can be seen from Fig. 1, when the sucker rods shift up and down, the oil is raised to the surface and the water is injected. Thus the downhole conditions allow rapid separation of oil and water. [12,13] Although it is difficult to maintain the system when the separation equipment is placed downhole, its economics makes this system attractive to the industry.

2.2.2 Produced water injection and re-injection

Produced water injection (PWI) and produced water re-injection (PWRI) are two water management techniques which have been applied to the oil and gas field because of their great environmental protection. PWI refers to disposal of the produced water to the formation /aquifer zone, whereas PWRI refers to sending back the produced water to the reservoir to keep the reservoir pressure constant.[12] For PWI and PWRI, it is extremely essential that produced water do not escape from the disposal zone and run into a sensitive aquifer or the surface. Sometimes this injection system becomes costly for the operator if the water disposal wells are not located on the same field.

2.3 Typical methods currently in use for treating produced water to remove oil from oil in oil water emulsion in the exploration and production (E & P) industry

To remove oil from produced water, various methods are in use in the exploration and production industry. Among them, the most popular are gravity settlement, hydrocyclone separation, centrifuge, particle coalescing, emulsion flotation.[11]

To follow is a brief description of above-mentioned treatment methods for produced water.

2.3.1 Gravity settlement

The main driving force for this separation method is the difference in specific gravity between oil and gas. This is the most widely used design approach.

2.3.2 Hydrocyclone separation

Using hydrocyclones for separation of dispersed oil from produced water has been a strong trend in recent years for operators and engineering contractors in E & P industries. They are simple and effective devices. A geometrically engineered hydrocyclone uses centrifugal separation and core reversal to eliminate oil from an oil-water emulsion feed stream and form two flow steams (oil and water).[15] Hydrocyclones operate at higher gravitational forces than conventional separators. These devices are very attractive for offshore applications for two reasons. First, they are compact and second, they are not susceptible to base movement. Fig. 2 schematically shows a hydrocyclone device. When a centrifugal force, which may be 1000 times the force of gravity, is applied to the oil- water feed stream, the water moves to the wall of the hydrocyclone, separating oil to the center of the device. [16]

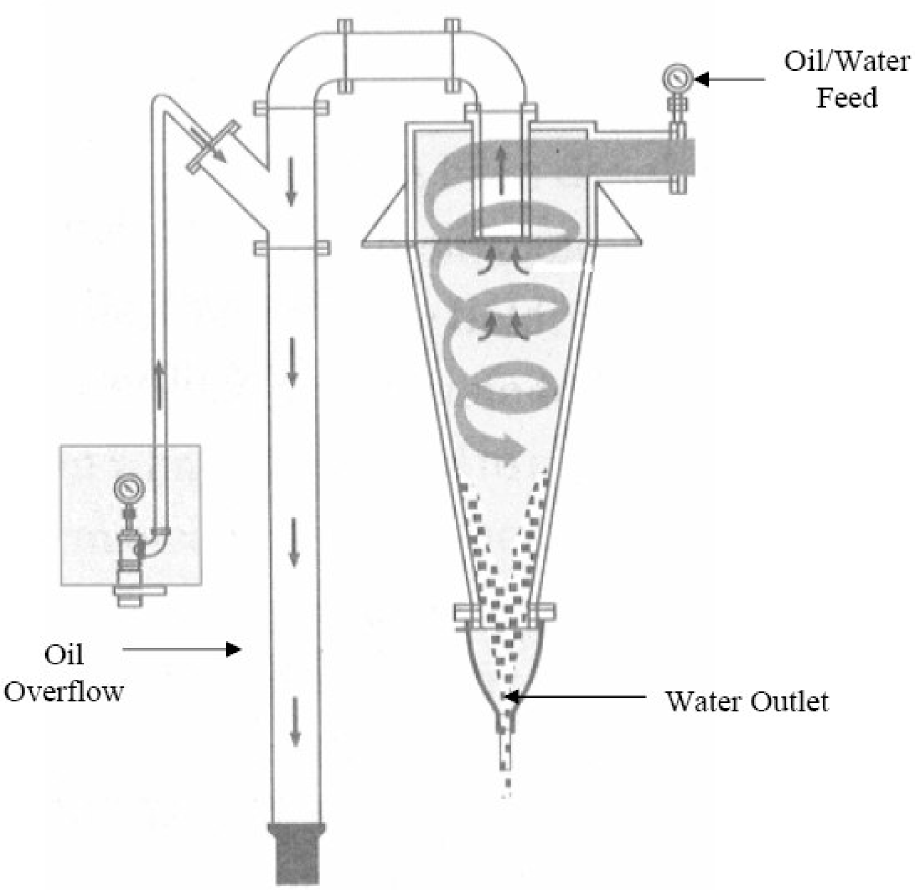


Fig. 2- Schematic diagram of hydrocyclone[12]

If the produced water characteristics are favorable hydrocyclones will give very low oil-in-water effluents (<20 ppm).[17] Favorable conditions means that the solution has to be hot, must include large droplet sizes (>10μm) and there must exist a considerable density difference between water phase and oil droplets. Centrifugal force is used in hydrocyclones to separate fluids of different specific gravity. Hydrocyclones operate without any moving parts. When Oil and water emulsion enters the hydrocyclone at a high speed from the side of a conical chamber, the subsequent swirling action causes the heavier water to move to the outside of the chamber and leave through one end. The lighter oil remains in the center of the chamber and exits through a second aperture. The water fraction which contain a low concentration of oil (typically less than 500 mg/L), can be injected and the oil fraction along with a little water is pumped to the surface One major disadvantage that has been observed for hydrocyclones is that they are not very effective at low pressure.[15, 16] Some other limitations include erosion due to high liquid velocities and failures of cones at welds and supports due to vibration. Moreover it is also found that hydrocyclones are not efficient if the oil droplet size distribution is less that 10 micron diameter.[16]

2.3.3 Centrifuge

The centrifuge is a bowl-shaped structure that includes a rotor. This rotor spins round at a very high speed.[17] After he oil water feed enters the centrifuge, the rotor forces it to spin. Centrifugal forces cause the heavier molecules to accumulate near the wall of the bowl and the lighter molecules will gather around the center of the centrifuge. Therefore it can be said that a centrifuge, more or less, follows the same operating concept as that of the hydrocyclones. Centrifuges are good at cleaning low pressure produced water and also for oily water streams from the drain system. Fig. 3 shows a schematic diagram of the centrifuge system.[18]

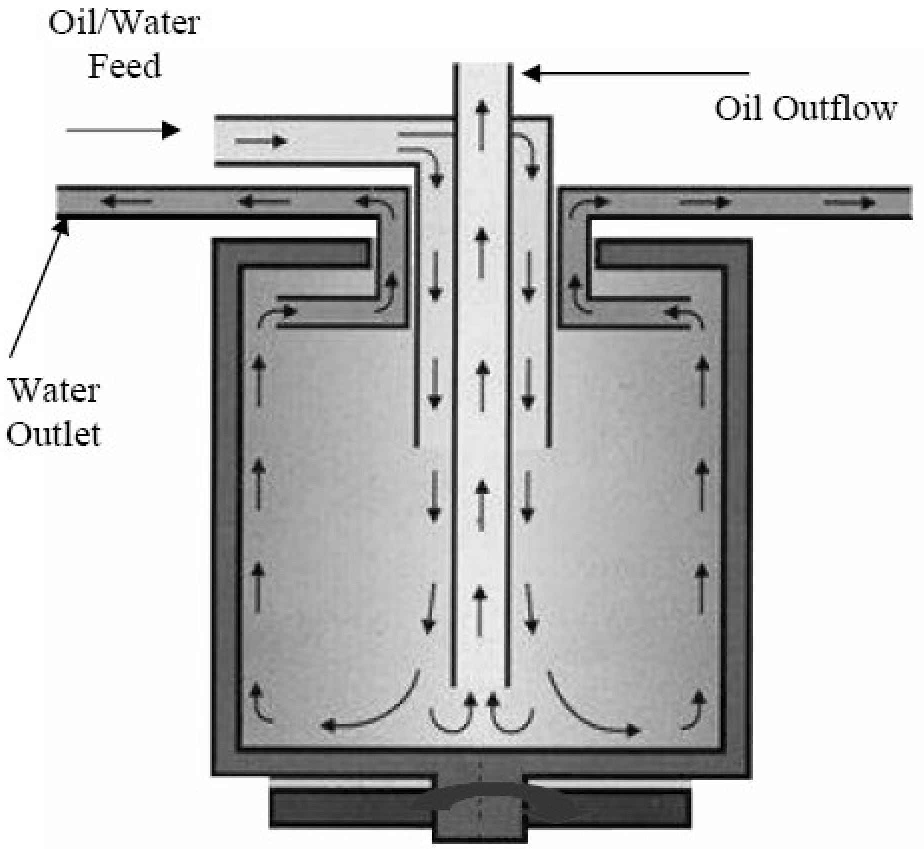


Fig. 3-Schematic diagram of centrifugal separator [18]

Because centrifugation requires high speed equipment, it is not suitable or effective for offshore application[11]. Moreover, if used for offshore application, disposal becomes a huge problem. Maintenance of centrifugation systems is a problem too. Rye and Esben found that after 2000 running hours, extensive chalk was built on the centrifuge disc plates and therefore they concluded that the maintenance for centrifuge system is a very time consuming event [19]. Therefore, this system of treating produced water can be a little disadvantageous. On top of these issues, it is very difficult to handle high pressure gassy water with this type of unit. For these reasons, centrifuge units are not widely used in offshore operations.[6]

2.3.4 Adsorption, an innovative and cost effective way of removing oil from the produced water

By now the reader is well aware of the typical methods of treating produced water currently in use and their working principles. As the reader may see that almost of them have limitations and above all they are costly. Therefore it is necessary to explore a different methodology to handle the produced water issue which is efficient as well as cost effective.[20] Adsorption can be such a method. As mentioned previously, the most preferred method of treating produced water will be the one which is efficient and conserves the environment in an economical way. From those points of view, adsorption can be a preferable method of cleaning produced water and therefore, the author would like to explore this method thoroughly.

The next chapter discusses this adsorption and its relevance in removing oil from produced water.

CHAPTER III

ADSORPTION CONCEPT IN REMOVAL HYDROCARBON REMOVAL PROCESS

3.1 Hydrocarbons present in water

For the last several decades, exploration and production (E&P) industry has been trying to develop efficient and cost effective methods to remove hydrocarbons from oil water emulsion. It has been found that one method alone is not sufficient to remove hydrocarbons to the desired level (29 ppm or less oil in water).[21] Typical hydrocarbons present in produced water include aliphatic, alicyclic and aromatic compounds. That's why a combination of various techniques have to be applied together to achieve the target level of hydrocarbon in produced water (i.e., 29 ppm or less oil in water). Individually these techniques may perform differently but when applied together, they act together toward treatment of the produced water. Depending on types of oil present in produced water, various methods of removing oil, such as adsorption, filtration, extractive, precipitation and oxidation, have been adopted to separate dissolved oil from oil water emulsion. Produced water primarily includes crude oil components. In some parts of the world, residual hydrocarbons from drilling mud components are also seen to be present in the produced water. But the major classifications of oil and grease that contaminate waters and ground waters are: [21, 22]

- Free oil and grease (FOG): These are oils that rise rapidly to the surface under steady conditions
- Mechanically emulsified oil: These are fine droplets of oil ranging in size from micrometers to a few millimeters
- Chemically stabilized emulsions: These are active on the surface and very stable due to interaction at the oil-water interface. The droplet size for this type is less than 20 µm
- Chemically emulsified or dissolved oil: These are finely divided oil droplets of 5µm diameter or less or individual molecules
- Oil-wet solids: This type of oil adheres to sediments or other particulate materials of waste water.

Emulsions were thoroughly discussed by George, *et al.* [23] These are defined as a heterogeneous system that is made up of at least one immiscible liquid thoroughly dispersed in another liquid in droplet form, whose average diameter size is more than 0.1µm. As soon as the droplets come close to each other, they have a tendency to coalesce and rise to the surface. Droplet size is one of the factors that determine the stability of the emulsion. George, *et al.*[23] mentioned that the smaller droplet size increases the stability of the emulsion. When the oil-water mixture is not emulsified, the oil floats on the top of the water as a slick or sheen. Emulsification can be achieved mechanically or chemically. A surfactant, which has a hydrophobic-oliophobic end and a hydrophobic-oleophilic-hydrophylic end, has to be added for chemical emulsification.

Both ends act as a coupling agent between oil-water phases. Emulsifiers having a polar end (i.e., it has a charge) and a non-polar end, prevent the oil droplets from coming close to each other and coalescing. Surfactants boost the stability of the emulsion because they pass on a like charge on the oil droplets, causing them to keep away from each other and scatter. [23] Mechanical emulsions can be made by stirring the oil-water mixture at a high speed. In the mechanical emulsion process, higher concentrated emulsions need higher rpm and time to make the emulsion stable.

3.2 Hydrocarbon removal with organoclay and its advantages

Produced water is a major source of oil-contaminated water. But it is possible to turn this huge volume of produced water into an economic asset and therefore the concept of using the treated water can be a great incentive. After proper treatment, produced water could be used for a beneficial purpose, such as irrigation or industrial use. Therefore the treatment process of produced water has the potential of converting a high cost liability into an asset. In fact, for the produced water to be used for beneficial purposes, it has to be free from its salt and oil components. Unfortunately, current technologies such as reverse osmosis or electro-dialysis are rendered ineffective by the residual oil present in the brine. Therefore most of these methods are not effective if used separately as they cannot remove hydrocarbons adequately and cost-effectively to make the produced water usable for beneficial purposes. Actually, the above mentioned methods of cleaning the brine have to be used together with some effective oil removal methods to completely clean the produced water and make it free from all the salt and oil impurities. Sadly enough, there is lack of efficient and cost effective oil removal methods which can be used together with conventional salt removal methods. This is a reason for which beneficial usage or discharge of produced water remains limited [24]. Therefore, it can easily be concluded that had there been a water treatment method to remove oil that is efficient, cost effective and is capable of meeting the compliances, better usage of the produced water would have been possible.

But there is good news too. There is a technique that shows ample promise to accomplish the treatment of produced water to remove oil with all the criteria mentioned in the last paragraph. This method is known as adsorption. Adsorption is very efficient, cost effective and most importantly has the capability of meeting the environmental compliance as far as the discharge standard of the oil content of the produced water is concerned.[25] Adsorption, as a method of produced water treatment, can clean produced water effectively by maintaining environmental compliance goals and hopefully at a minimal cost.

Adsorption can be carried out using many types of adsorbents. One of these many types of adsorbents is granular activated carbon (GAC) which has been widely accepted by E&P industry for quite a long time for removing hydrocarbons from waste water by adsorption. Organoclay has emerged as a better substitute for this GAC. In fact, studies show that if a comparison is made between the organoclay and GAC, organoclay has several advantages over the GAC as an adsorbent.[21] It has been seen that if organoclay is used as a pre-polisher for removing small amount of oils from industrial processing water, it shows better performance as far as the removal of hydrocarbons is concerned. Moreover, it is found that, depending on the kind of oil being treated, the removal process with organoclay can be quantified as seven times more effective as GAC as far as the removal rate is concerned.[24] To follow is a brief outline of some of the advantages of using organoclay over GAC: [1, 23]

- Organoclay has higher adsorption capacity than GAC and can adsorb 60-70% hydrocarbon by weight.
- It is very effective in removing insoluble and dispersed hydrocarbons.
- It does not desorb the adsorbed hydrocarbons.

Organoclays can be used to remove mechanically emulsified oil from water to desired level of discharge water. Although organoclays can be used in cleaning up of storm waters, boiler steam condensates, ground water, landfill leachate, boiler feed water, wood treating water and produced water from oil production wells, the two most common applications at this time are [20,23]:

- As pre-treatment for granular activated carbon, reverse osmosis (RO) units and ultra filtration (UF) units, ion-exchange resins, where the purpose of the organoclay is to increases the life and use of the above mentioned media by preventing blinding and fouling.
- As a post-polisher for oil - water separators

In the next section, a detailed description of the working principle of the organoclay will be given

3.3 Working principle of organoclays

In this section, a description of the working principle of the organoclays will be given. But before that, to understand the basic physical structure of the organoclay, it is important for the reader to have some idea about bentonite and quaternary amine. According to Wikipidia [26], bentonite can be defined as an aluminium phyllosilicate absorbent which generally contains impure clay consisting mostly of montmorillonite, $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2\cdot(H_2O)_n$. Two types of bentonite are available, swelling bentonite which is also called sodium bentonite and non-swelling bentonite or calcium bentonite. Bentonite is formed from weathering of volcanic ash, most often in the presence of water.

And quaternary amines can be defined as "a cationic amine salt in which the nitrogen atom has four groups bonded to it and carries a positive charge". [27] Quaternary amines are used as oil-wetting agents, corrosion and shale inhibitors and bactericides.

After giving the brief description on the bentonite and quaternary amines, it's time to get back to the organoclays. Organoclays are manufactured by modifying bentonite with quaternary amine containing a nitrogen ion at the end. The nitrogen end of the quaternary amine is positively charged. It is hydrophilic and therefore ion exchanges onto the clay platelet for sodium or calcium. Bentonite, which typically has charge of 70-90 meq/g is a chemically modified volcanic ash and consists of montorillonite and after alteration with quaternary amine, 30-40 meq/g of charge remains in it which allows it to remove small amount of heavy metals.[23,24]

As soon as organoclay is introduced into water, its quaternary amine becomes activated and opens out perpendicularly off the clay platelets into the water. A Cl^- or Br^- ion is loosely attached to the carbon chain. So, after being replaced by the sodium ion and getting bonded with Cl^-, sodium salt is produced. Now, the oliphilic end of the amine dissolves into the oil droplet and removes the droplet from water by adsorption.[23] This phenomenon occurs into the pores. Partition reaction also takes place at the outer side of the clay. So, it is clear that adsorption comes into play in the overall removal process. [23]

It has been found that when long chain amines dissolve into the oil or hydrocarbons and due to electrostatic force they have the ability to hold or fix in the droplets. This activity occurs on the surface of the clay platelet. For their porosity, the oil droplet or other organics are adsorbed into the pores of activated carbon. One may wonder what will happen if an oil droplet has a larger diameter than the diameter of the pores. In that case, the oil drop will simply sit on top of the pore and thus will prevent further adsorption. In the next subsection, this adsorption phenomenon will be discussed in detail.

3.3.1 Principles of the adsorption process

3.3.1.1 Surface interaction

Adsorption at a surface is the result of binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface. These forces originated from electromagnetic interactions. Ion exchanges, physical, chemical and specific are the four major types of adsorption[25].

Ion exchange adsorption is electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent. Physical adsorption results from the action of Van der Waals force. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The chemiosorptive bond is usually stronger than that derived from the physical Van der Waals forces.[25] When attachment of adsorbate molecules at functional groups adsorbent surfaces result from specific interactions which do not result in adsorbate transformation is designated as specific adsorption.[25]

Adsorption from emulsion onto a solid can take place as a result of one or both of two characteristic properties for a given solvent adsorbate-adsorbent system. Solvophobic or lyphobic character or a particular affinity of the adsorbate for the surface of the adsorbent of the adsorbate is the primary driving force.[25] Adsorbate and adsorbent properties have a great impact on the adsorption process.[25]

3.3.1.2 Adsorbate-solvent properties

An inverse relationship between the extent of adsorption of a substance from a solvent and its solubility in that solvent can be generally anticipated.[25] For example, the water solubility of organic compounds within a particular chemical class decreases with increasing molecular size or weight because the compound becomes more hydrocarbon like as the number of carbon atoms increases. Thus, as the molecular weight increases, adsorption from aqueous emulsion increases. Molecular size can also affect adsorption rates if these are controlled by intraparticle diffusive mass transport within porous of the adsorbents, which generally is more rapid the smaller the molecule.[24] It must be accentuate that rate dependence on molecular size can be generalized only within a particular chemical class or homogeneous series. Large molecules of one chemical class (i.e., alkanes) may adsorb more rapidly than smaller ones of another if higher energies or driving forces for adsorption are involved. Certain chemical and physical properties of a compounds change upon ionization, and this can affect adsorbability.[25] Most observations for amphoteric substances point to the generalization that as long as the adsorbing compounds are structurally simple and electrostatic or exchange reactions are not significant, adsorption from polar solutes such as water is greater for neutral species that for the corresponding ionic forms. As compounds become more complex the effects of ionization decrease. Polarity also affects the adsorption process. A polar solute will be strongly adsorbed from a non-polar solvent by a polar adsorbent, and, at the opposite end of the spectrum, will prefer a polar solvent to a non polar adsorbent.[28]

Adsorption reactions are normally exothermic. The equilibrium extent or capacity of adsorption in a given system is found to increase with decreasing temperature. Conversely, because adsorption kinetics is generally controlled by diffusive mass transfer, rates of approach to equilibrium normally increase with increasing temperature.[25]

3.3.1.3 System properties

Adsorption of ions may be influenced by solution pH. To the extent to which adsorption differs between the conjugate forms of acidic or basic compounds, pH affects adsorption in that it governs the degree of ionization of such compounds.[25] The components of a mixture of adsorbates may mutually enhance adsorption, act relatively independently, or interfere with one another. Mutual reduction of both adsorption capacities and adsorption rates can be expected if the affinities of the adsorbates do not differ by orders of magnitude and if there are no specific interactions among them which enhance adsorption; this because the adsorption of more than one substance generally reduces the number of surface sites available to each.[24] For diffusion controlled rates of adsorption by porous adsorbents, very slowly diffusing species in mixed adsorbate systems can depress rates of uptake of those which diffuse more rapidly. Adsorption kinetics is the reason for this process.[24, 25]

3.3.1.4 Adsorbent properties

Adsorption is a surface phenomenon. Therefore practical and commercial adsorbents are characterized by large surface areas, the majority of which is comprised of internal surface bounding the extensive pores and capillaries of highly porous solids. Activated carbon is one of the most widely used porous adsorbents because of its capability for efficiently adsorbing a broad range of different types of adsorbates.[25] While activated carbon’s wide spectrum adsorption capability is unmatched by any other material, certain synthetic adsorbents such as organoclay may offer distinct advantages in specifically defined cases.

The performance characteristics of adsorbents relate in a large measure to their intraparticle properties. Surface area and the distribution of area with respect to pore size generally are primary determinants of adsorption capacity.[25]

3.3.2 Adsorption equilibria

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases when the system reaches equilibrium; that is, when no further net adsorption occurs. The common manner in which to depict this distribution is to express the amount of substance adsorbed per unit weight of adsorbent, q_e, as a function of the residual equilibrium concentration, C_e, of substance remaining in the solution phase. A expression of this type, termed an adsorption isotherm, defines the functional distribution of adsorption with concentration of adsorbate in solution at constant temperature. Typically, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion.[25,28]

Several equilibrium models have been developed to describe adsorption isotherm relationships. To follow is a description of the most commonly followed equilibrium models.

3.3.2.1 Langmuir model

This model originally developed for adsorption of gases onto solids, assumes that adsorption energy, expressed as joule/moles, is constant and independent of surface coverage; that adsorption occurs on localized sits with no interaction between adsorbate molecules, and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate.[23] The relationship can be derived by considering the kinetics of condensation and evaporation of gas molecules at a unit solid surface. So at equilibrium rate of Evaporation and rate of condensation become equal. [28]

$$k_d = k_a P(1-\theta) \text{ ………………………………….. (1)}$$

Where, θ = fraction of surface coverage.

P = absolute pressure of gas. (psi)

k_d = Rate constant for evaporation (no. of molecules evaporate/time)

k_a =Rate constant for condensation (no. of molecules condensate/time)

Again, $$\theta = \frac{k_a P}{k_d} + k_a P \text{ …………………………………….. (2)}$$

$$= \frac{bp}{1+bp} \text{ ……………………………………….. (3)}$$

where, $b = k_a / k_d$, is related to the enthalpy of adsorption.

For solid –liquid system the equation is written as:

$$q_e = \frac{Q^* b C_e}{1+bC_e} \text{ ………………………………………………….(4)}$$

Where, q_e = amount of solute adsorbed per unit weight of adsorbent (mg/gm)

Q^*= solid phase concentration corresponding to complete coverage of available sites (mg/gm)

C_e= Residual liquid phase concentration at equilibrium. (mg/l)

So, after rearranging the equation becomes, [28]

$$q_e = Q^* - \frac{q_e}{bC_e} \quad \text{……………………………………………………… (5)}$$

It is to be noted that the parameters in the above equation (i.e., b and Q^*) vary with temperature and the specific chemistry of the solution or gas and the surface. For example, in liquid –solid systems Q^* and b determined for a certain adsorbent and adsorbate wll generally be a function of temperature, pH, ionic strength, and so forth.

3.3.2.2 BET model

Limitations of Langmuir isotherm model were reduced by the BET (Brunauer, Emmet and Teller) model. The essential assumptions of this model are that any given layer need not be complete before subsequent layers can form, that the first layer of molecules adheres to the surface with energy comparable to the heat of adsorption for monolayer attachment, and that subsequently layers are essentially condensation reactions. If the layers beyond the first are assumed to have equal energies of adsorption the BET equation takes the form: [28]

$$q_e = \frac{BC_eQ^*}{(C_e - C_s)\left[1 + (B-1)\frac{C_e}{C_s}\right]} \quad \text{……………………………… (6)}$$

Where, C_s =Saturation concentration of the solute (mg/l)

B= BET isotherm constant.

Q^*= solid phase concentration corresponding to complete coverage of available sites. (mg/gm)

3.3.2.3 Freundlich model

Despite the sound theoretical basis of the Langmuir, BET models, these isotherms often fail to describe experimental data adequately.[25] Freundlich (1926) found that adsorption equilibrium data were often better described by the relationship

$$Q_e = K_f C_e^{1/n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where, K_f and $1/n$ are characteristic constants. Freunlich attempted to attach rigorous physical significance to the parameters K_f and $1/n$. The value of K_f can be taken as a relative indicator of adsorption capacity, while n is indicative of the affinity of the adsorbate for the surface (adsorbent).

3.3.3 The Adsorption isotherm

The adsorption isotherm is the initial experiment test step in an evolution to determine feasibility of adsorption treatment and whether further test work should be conducted. The adsorption isotherm is constructed with data obtained from the equilibrium test which provides data on adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in solution.

The equation that expresses the equilibrium between the adsorbate adsorbed per unit weight of carbon and the concentration of adsorbate remaining unabsorbed in the Freundlich equation can be stated as: [25, 28]

$$Q_e = \frac{x}{m} = K_f C_e^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where x is the amount of organic adsorbed (mg/gm), m the unit weight of organoclay, C_e the equilibrium concentration remaining in the solution, and K_f and n are the constants specific to the adsorbate of concern.

$$Log\frac{x}{m} = LogK_f + \frac{1}{n}LogC_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

This expresses the equation for a straight line when x/m is plotted vs. C_e. The resulting line has a slope of $1/n$ and an intercept of K_f when $C_e = 1$. The x/m and C_e values are measured and calculated from the isotherm test while plotting the test data allows determination of $1/n$ and K_f.[28]

3.3.4 Factors affecting the isotherm

3.3.4.1 Adsorbent preparation and dosage

The adsorbent to be tested should be of same mesh size. While any particle size of the same adsorbent should reach the same equilibrium capacity, the rate at which the adsorbent reaches equilibrium is dependent on the particle size. Smaller particles simply reach equilibrium faster that larger ones.

3.3.4.2 Hydrogen ion concentration (pH)

Adsorption from solution can be highly pH dependent. From an economical and practical standpoint, fluid should always be evaluated at the ambient pH.[25]

3.3.4.3 Temperature

Temperature affects the adsorption process. Isotherms generally are conducted at the temperature which is expected in the treatment process. It is recognized that an elevated temperature generally provides a faster rate of diffusion of the impurities into the adsorbent pores while simultaneously potentially changing the equilibrium capacity of the adsorbent for the adsorbate.[25]

3.3.4.4 Contact time

To approach equilibrium with the adsorbate, sufficient contact time between the adsorbent and the fluid is necessary to allow the adsorption. Each adsorbent particle has to purify a certain volume of liquid, so that the higher adsorbent dosage with less volume to treat per unit weight may reach equilibrium somewhat faster than the low dosages.[23] Consequently, enough time must be permitted for the critical low carbon dosage to yield valid data points.[25] Generally 4-5 hrs contact time with vigorous agitation is sufficient for approaching equilibrium but this can vary with the sample. Measuring the concentration change over time in a particular system will show the effect of contact time. The equilibrium concentration can be achieved by plotting change of concentration vs. time graph.[25]

CHAPTER IV

OBJECTIVES AND METHODOLOGY

4.1 Research objectives

The objectives of this research are

- To investigate the potential of granular organoclay to remove oil from an oil-in-water emulsion
- To predict the batch kinetics and adsorption isotherm to evaluate the adsorption capacity of the organoclay and to develop a kinetic model that will show the time dependency of adsorption equilibrium concentration.

4.2 Methodology

To satisfy the research objective, following procedures were applied:

1. First of all, it was necessary to select the type of oil using which the experiments would be conducted. The particular type of oil that was chosen was SAE 30 motor oil. The rationale behind choosing this oil was that it was less volatile compared to other oils, particularly crude oil. Moreover, from experience of one of the research projects conducted in the lab showed that this oil gave the best calibration performance in the TD-500^{TM} fluorometer, an instrument that was used in this research project to measure oil concentration. Also the adsorption characteristics for

the organoclay are assumed to be the same for any oil that are of similar characteristics of SAE 30.

2. Emulsions with different level of concentrations were prepared in a plastic bucket by mixing the SAE 30 motor oil and water. Each bucket contained 3 liter of emulsion. A specified amount of organoclay, contained in a small cotton pouch, was put inside the oil-water emulsion mixture. Loading capacity of oil dictated the amount of organoclay to be put in the emulsion in each plastic bucket. The ratio of the oil to organoclay was 1:2 on a mass basis (gm/gm) and this ratio was always kept constant. Continuous stirring (1500 rpm) was required to keep the emulsion homogenous. After a certain time interval, data was collected to measure the concentration of oil in the emulsion. A similar procedure was applied to collect data from emulsions of various concentrations, from which adsorption patterns could be identified and a model could be developed. It must be mentioned here that, while measuring the amount of oil adsorbed by the organoclay, the author particularly considered the amount of oil lost in evaporation, the amount of oil adsorbed by the cotton pouch and any oil that may have lost in the surface of the plastic bucket. This was done by employing three buckets. The first bucket contained organoclay in a pouch immersed in oil water emulsion. The second bucket contained oil water emulsion and a pouch immersed in it. The pouch was left empty with no organoclay inside it. The third and final bucket contained only oil water emulsion. Reading from the third bucket, therefore, gave the amount of oil lost due to evaporation and plastic bucket. Let this amount be x gm. Amount of oil lost due to the combined effect of evaporation and

absorption by cotton of the pouch and plastic bucket could be determined from the second bucket. Let this amount be y gm. Oil lost due combined effect of adsorption of organoclay, evaporation and absorption by the cotton of the pouch and plastic bucket could be determined from the reading obtained from the first bucket. Let this amount be represented by z. Then, the amount adsorbed by the organoclay only would be p = z-x-(x-y). This amount p thus considers the oil adsorbed by the organoclay in SAE 30 oil water emulsion. This procedure, thus, gave the author a high confidence level of data collection regarding the oil adsorbed by the organoclay. This method can be clearly understood from the sample calculations given in section 6.1.2

3. First order adsorption isotherm model was also developed to examine how the adsorption capacity varies for different values of equilibrium concentration. From this model, adsorption parameters were calculated.
4. The next step was to predict the kinetic behavior of the adsorption of oil water emulsion by the organoclay. To accomplish this task, adsorption data with respect to a certain time interval were gathered and put into graphical representation. This allowed the author to observe a pattern which could be used to predict the kinetic behavior of the organoclay.

CHAPTER V

REMOVAL OF HYDROCARBON FROM OIL-WATER EMULSION

5.1 Quantification of HC content in oil-water emulsion

An organic compound is a member of a huge class of chemical compounds whose molecules contain carbon, with the exception of carbides, carbonates, carbon oxides and elementary carbon. It is common knowledge that organic compounds are defined as substances that contain carbon. Among the organic compounds, hydrocarbons (HC) are the simplest. HC contain only carbon and hydrogen having straight-chain, branched chain, or cyclic molecules. Different hydrocarbon molecular structures are formed by attaching different functional groups to the carbon chain.[29] Hydrocarbons are very common in the environment. Various types and amounts of hydrocarbons are present in oil field brine. These hydrocarbons exist in oil field brine as emulsified, free floating, dissolved or as a suspended hydrocarbon solid.

There are many techniques available to measure the hydrocarbon levels in the water. Hydrocarbon extraction is the most important step for measuring HC levels. EPA and other regulatory agencies have some restrictions against some of these extracting processes. For example, Freon used to be used for extraction of HC from water solution, but it has been proved that Freon can cause atmospheric ozone layer depletion and thus has bad impact on the environment. So it is recommended that n-hexane be used in the extraction process instead of Freon.[12]

The TD-500™ is a fluorometer which is devised for quick, easy and accurate measurement of crude oil and gas condensates in water. For clarity, a definition of condensate seems to be appropriate here. Actually a condensate can be defined as "a low-density, high-API gravity liquid hydrocarbon phase that generally occurs in association with natural gas." [27] After calibration with a known standard, the TD-500™ can be used to determine concentrations of unknown samples. This TD-500™ uses fluorescence technique to assess each sample. Ultraviolet light source is used in the method and instead of measuring the actual adsorption, fluorescing characteristics of specific compounds are observed. Fig. 4 shows the TD-500™, hydrocarbon analyzer that is generally used for measuring the HC content. This TD-500™ HC analyzer was also used for measuring HC content research project.

Fig. 4- TD-500™ by Turner designs hydrocarbon instruments [12,30]

In the fluorescence phenomena, a fraction of the adsorbed wavelength in the targeted compound is re-emitted at a higher wavelength. When florescent light is passed through the solution to be examined, water molecules, at a specific wavelength of UV light, get excited while certain compounds including hydrocarbons starts absorbing energy. Very few compounds will re-emit this light at a higher wavelength. Hydrocarbons are among those which re-emit at a wavelength range that is very unique to them. Concentration or ppm levels of hydrocarbons can be determined by measuring the fluorescence intensity of the re-emitted wavelength.[12] This methodology makes the device very selective to hydrocarbons. According to the manufacturer of the TD-500™ instrument, it has the following features:

- Sample can be analyzed in less than 4 minutes
- Easy calibration
- No solvent loss due to evaporation during measurement.
- Minimum detection limit is less than 1ppm for oils
- Precise and extremely repeatable data
- Correlates to standard laboratory gravimetric and Infra Red (IR) methods

Performance of various removal techniques in terms of efficiency and oil removal capacity can be estimated from hydrocarbon analysis or Total Organic Carbon (TOC) analysis of oil water emulsion. TOC also can be defined as the amount of hydrocarbons in the given sample that liberate carbon dioxide upon oxidation in an acidic solution.[12] It is important for the reader to understand that the reading for various concentrations that were collected in this research project were actually TOC data obtained from the TD 500^{TM} instrument. Hydrocarbon analysis or Total Organic Carbon (TOC) analysis of samples containing oil help to evaluate the performance of the removal method in terms of efficiency and oil removal capacity. As mentioned before, TOC actually reveals the amount of hydrocarbon in a given sample that release carbon di-oxide upon oxidation in an acidic solution. Since oil is a hydrocarbon and is of paraffinic (C_nH_{2n+2}) origin, through TOC measurement, the amount of oil (or hydrocarbon to be precise) in a given sample can be determined which is based upon a chemical oxidation that release carbon di-oxide. Thus by using TD-500^{TM} instrument, amount of oil in an oil water solution/emulsion can be determined by TOC analysis. It should be mentioned here that, before a TD-500^{TM} can be used for determining the amount of oil in a particular oil water emulsion, the instrument or analyzer needs to be calibrated according to the oil to be examined and this calibration process is very vital in making a true analysis of the specified oil. Following section enumerates the calibration process of the TD-500^{TM} HC analyzer performed in this research project.

5.2 Calibration method

As mentioned in the previous paragraph that calibration of the fluorometer TD-500^{TM} HC analyzer has to be done in order to obtain any meaningful results from the experiments conducted. The calibration process was conducted in several steps and these steps are described below.

STEP 1:

First, density (gm/ml) of the oil that would be used (SAE 30 motor oil in this case) should be determined. This can be done by measuring volume (using pycrometer) and mass (using gravimeter).

STEP 2:

The next step is to prepare the oil-water emulsion of the desired concentration. It is to be mentioned here that, the desired concentration level chosen for the oil water emulsion was 1000 ppm. At this point, it was also required to decide how much oil-water emulsion was to be prepared. For this particular research project, the amount of oil-water emulsion that would be prepared was 3.0 liters.

STEP 3:

Having known the required amount and the desired concentration of oil water emulsion, the next thing that needed to be done was to find out how much oil was required to prepare the above mentioned 3 liter oil-water emulsion of 1000 ppm concentration. This was easily determined by using the following expression:

$$m_o \ (in\ grams) = \frac{C_o \times V}{1000} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where, m_o = Oil Wt. (Oil requirement in grams)

C_o = Concentration of oil water emulsion (in ppm)

V= Volume of the oil water emulsion (in liters)

The right hand side of the above expression was divided by 1000 to get the oil requirement in terms of grams.

STEP 4:

The next task was to find out the volume of oil that was required to prepare 3 liters of oil-water emulsion of 1000 ppm concentration and was found by using yet another expression like the following:

$$V_o = \frac{m_o}{\rho_o} \quad \text{……………………………………………………………} \quad (11)$$

Where, V_o = Required Oil volume to prepare oil water emulsion (in ml)

m_o = Oil Wt. (Oil requirement in grams). This amount was obtained from Equation 10

ρ_o = Density of oil (in gm/ml)

Now, to make the emulsion, water in plastic bucket was placed in an ice bath and the required oil (obtained from equation 11) was added to the bucket with continuous stirring for 20-30 minutes. It was extremely important that the bucket be covered properly to prevent any loss due to evaporation. 20-30 minute of continuous stirring at 1500 rpm was recommended for obtaining a homogeneous emulsion.

One important concern for TD-500^{TM} HC analyzer was that, it could not measure the oil concentration straight out of an oil water emulsion. Rather it used extracted oil for measuring oil concentration of an emulsion. Therefore to calibrate the TD-500^{TM}, it was not possible to use oil water emulsion. Rather extracted oil was used. Therefore, oil had to be extracted from the emulsion in some fashion. This was carried out in step 5.

STEP 5:

In this step, oil was extracted from the previously prepared oil water emulsion. 300 ml beaker was used to retrieve samples out of the 3 liter oil-water emulsion. It was important to collect all the samples at the same time to obviate any temporal effect. Four graduated cylinders (GC) were used to collect the emulsion samples. After collecting 90 ml of emulsion sample, it was placed in GC 1. Similarly a 67.5 ml sample was placed in GC 2. 45 ml and 22.5 ml emulsion were placed in GC 3 and GC 4 respectively. Remaining volume of the GCs was filled with pure water to make the total emulsion 90 ml. After water was added to all the GCs, their levels of concentration were definitely changed. GC 1 represented 1000 ppm emulsion; GC 2 represented 750 ppm whereas GC 3 and GC 4 represented 500 ppm and 250 ppm emulsion respectively.

STEP 6:

The next task was to extract oil from each of these emulsion samples from all the GCs. To do this, each emulsion samples were transferred to different separatory funnels (SF). 10 ml of n-hexane and 4-5 drops of 32% hydrochloric acid had to be added in each of the separatory funnel. Thus pH level in each SF was lowered below 2 when hydrochloric acid or sulfuric acid was added. The ratio of n-hexane and sample per volume was always kept constant and the value of this ratio was 1:9. Then these emulsions in each of the funnel were swirled gently and were kept idle for 5 minutes. In this time, oil and water became separated in two different layers where the top layer contained desired extracted oil and the bottom layer contained water. The bottom layer was drained through the attached valve and the extracted layer was discharged in the appropriate beaker which should be from 2 to 3 milliliters. Thus, 4 small beakers containing all the extracted layers from different concentrated emulsions were obtained.

STEP 7:

After completion of the calibration procedure, each sample was analyzed. A clean pipette was used to get the extract and set it into a clean minicell cuvette or 8 mm round cuvette. It was important to fill at least half of the cuvette with sample. The small cuvettes, containing the extracted layers sample were placed in TD 500^{TM} analyzer for analyzing the extracted layers of known concentrations. TD-500^{TM} analyzer measured the concentration of the extracted layers in ppm and gave the reading directly. These readings were compared against the known concentration values of the extracted layers.

This procedure was carried out for all the extracted layers contained in all the beakers and the collected readings from the TD-500™ analyzer were plotted in a graph along with the known concentration data. Each trial for measuring concentration in TD-500™ analyzer was conducted at least 4 times to ensure the repeatability of the reading. Moreover, scheduled calibration was essential to make sure that correct sample readings are being accomplished.

Fig. 5 shows the calibration curve for TD-500™ analyzer. Readings from the TD 500™ analyzer are plotted against the corresponding values of known concentration. As the reader may see that the difference between the readings of the TD-500™ analyzer and the actual values are very minimal and TD-500™ analyzer could be used with 99.4 % confidence for the particular oil water emulsion.

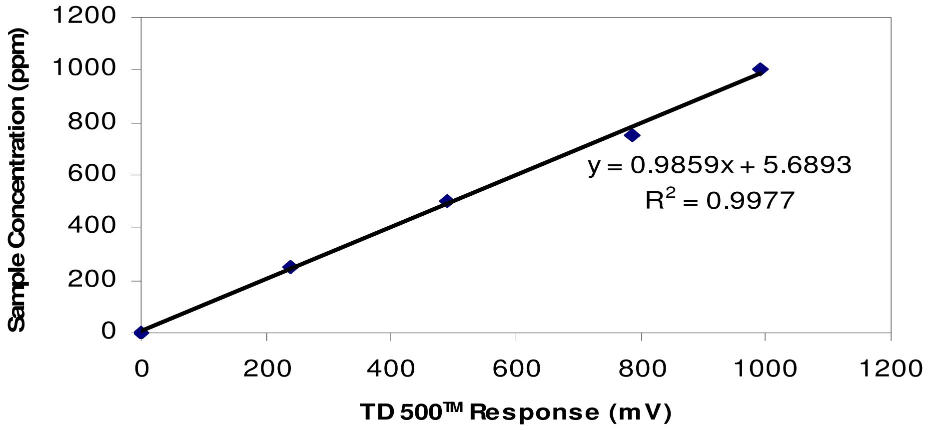


Fig. 5- Calibration curve for TD-500™ with SAE 30 motor oil

After the calibration of the TD-500^{TM} analyzer was completed and the confidence level of the readings obtainable from the device was determined, the next step was to conduct experiments to measure the adsorption capacity of organoclay. To follow is a detailed description of the methodology, set-up and procedures of experiments conducted for the measurement of adsorption capacity of organoclay.

5.3 Adsorption capacity experiments

Several experiments were performed with SAE 30 motor oil to measure the adsorption capacity of organoclay. As mentioned in the previous section, oil-water emulsions of 4 different concentrations (750 ppm, 1000 ppm, 1500 ppm and 2000 ppm) were prepared for performing the experiments to get the true picture of the adsorption capacity of organoclay in the oil-water emulsion. The particular type of organoclay that was used for this research project was PS-12385. This clay was supplied by Polymer Ventures Inc. The ratio between the amount of oil present in the oil-water emulsion and the amount of PS-12385 organoclay was always kept constant at 1:2 in oil-water organoclay system.

The 1:2 ratio was chosen because it was always desired that in the oil water organoclay system, the amount of organoclay were more than the amount of oil present in the emulsion. If one chose a 1:1 ratio of organoclay to oil, there was a possibility that the amount of organoclay might not be enough to adsorb all the oil. But if the amount of organoclay was kept more than the amount of oil present in the system, it was more or less ensured that enough organoclay would be available in the system to adsorb all of the oil present in the oil-water emulsion. That's why a ratio of 1:2 for oil to organoclay was chosen so that the oil water organoclay system used in this research project would not run into the problem of not having enough organoclay material to adsorb oil contained in the oil water emulsion. Moreover, this 1:2 ratio of oil to organoclay was kept constant for the entire oil water organoclay systems used in the experiments so that the author could compare different sets of adsorption data and predict the adsorption capacity and kinetic behavior of the organoclay.

In the next section, the methodology and the experimental procedures will be discussed.

5.4 Methodology and procedure

When organoclay is in a crushed state, its adsorption characteristics improve due to smaller particle size. One may wonder if smaller particle size improves the adsorption characteristics, why not use the organoclay in powdered form. The reason behind not choosing the organoclay in powdered form was that it was possible for the organoclay powder to get in to the pores of the cotton cloth of the pouches. In that case, the organoclay would have clogged the surface of the pouch and the overall adsorption process would have been hampered. Therefore, crushed organoclay, instead of powdered form, was used in all the experiments conducted in this research project. The physical properties of PS-12385 organoclay are given below: [12]

Appearance: Gray to Tan Granules

Bulk density: 45 lbs/ft^3

Granular size: 16/50 U.S. Sieve Size.

Dosage: The loading amount of organoclay depends on the concentration of the contaminant, contact time and fluid temperature. Typically, lower concentration of contaminants, lower solubility in water, longer contact time and moderate fluid temperature are favored for the treatment process.

The experience of the author of this thesis with PS-12385 organoclay has shown that, if it is presoaked in water for some time, the clots within the granular structure of organoclay are eliminated and its adsorption efficiency increases. Therefore the author decided to presoak the organoclay before using them for experiment conducted in this research project. In fact, the organoclays were presoaked in water for 24 hours before conducting any kind of experiments with them. To do this, specified amount of organoclay, according to the previously mentioned ratio (1:2) was measured and was put into a small cotton pouch. This cotton pouch was immersed into a beaker of water for the organoclay to be soaked with water.

To predict the adsorption capacity and kinetics of organoclay and also to reduce the loss of organoclay into the emulsion, it was important to put the organoclay in the cotton pouch. The material of the cotton pouch was selected such that the mesh size of the cotton pouch was smaller than the size of organoclay particles and therefore clay particles could not get out of the pouch. This unique arrangement of placing organoclay inside the pouch allowed oily emulsion to make contact with the organoclay. One more advantage of this cotton pouch was that it could move freely in the emulsion and hence a better contact with the oily emulsion was possible. It should be mentioned here that it was very important to cover the emulsion in the bucket with a lid to reduce the evaporation process. After a certain time interval, samples were collected from each bucket using a pipette. Fig. 6 schematically shows the experimental procedure with cotton pouch immersed in oil-water emulsion.

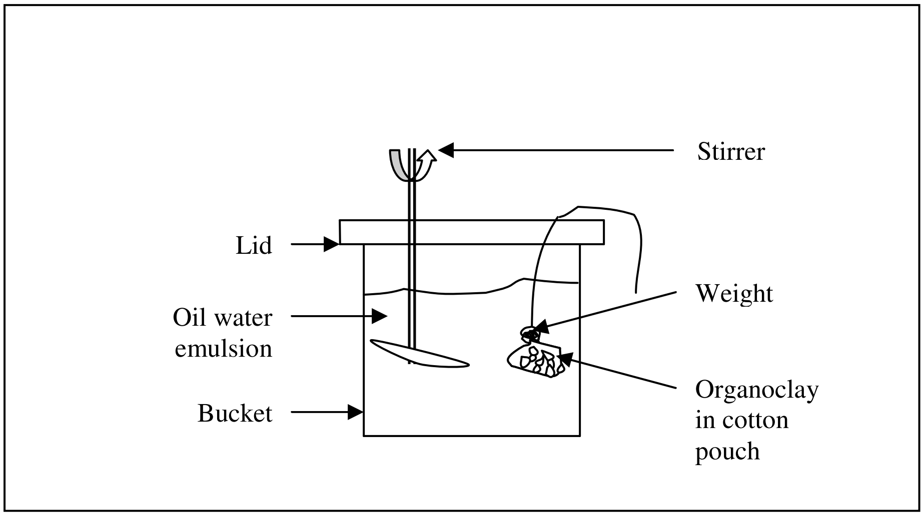


Fig. 6- Schematic diagram of adsorption kinetics experiment

Emulsion concentration, time of the experiment and the emulsion agitation (1500 rpm) were kept constant to get the exact adsorption behavior of the organoclay in oil-water system. After a definite time interval, a sample of oil-water emulsions was taken and analyzed with the TD-500^{TM} to measure the bucket concentration of the oil-water emulsion. To get the actual value of the adsorption capacity, evaporation or adsorption in plastic walls of the oil-water emulsion and surface adsorption of cotton pouch were considered for each sample calculation. A material balance of the emulsion was also conducted. All the experiments were carried out for 8 hrs.

The next section will be dedicated to describe the experimental set up used in this research project.

5.5 Experimental setup

Fig. 7 shows the experimental set up used in this research project.

Fig. 7- Experimental set up.

Fig. 7 shows three stand-alone stirrers at a time were used to conduct the experiments. The three plastic buckets represented following three different situations:

Bucket 1: Pre- soaked organoclay in a cotton pouch and a emulsion of oil- water emulsion of a specific concentration.

Bucket 2: An empty cotton pouch in a specific concentrated emulsion to measure the amount to oil absorbed by the cotton pouch itself.

Bucket 3: A specific concentration oil-water emulsion to measure the evaporation and adsorption of the oil onto the walls of the plastic bucket.

The experiments in this research project were conducted using plastic buckets. Oil may get stuck in the surface of these plastic buckets, therefore further research is recommended where glass buckets may be used and examine if using glass buckets make any difference in the adsorption capacity of organoclay.

With the experimental set-up mentioned above, all the experiments were conducted and results were recorded. A detailed description of the results obtained through conducting the experiments is given in the next chapter.

CHAPTER VI

RESULTS AND DISCUSSION

This chapter presents the results obtained by conducting various experiments and their interpretation and significance regarding the adsorption capacity, adsorption isotherm and kinetic behavior of organoclay in SAE 30 oil- water emulsion.

To satisfy the objective of this research project, three tasks were required to be accomplished and they were as follows:

- Finding the adsorption capacity of the organoclay
- Developing an isotherm model (Freundlich isotherm model)
- Finding the kinetic behavior of the organoclay in oil-water emulsion

The results obtained by conducting experiments were used to accomplish the above mentioned tasks using organoclay for a particular system of SAE 30 oil-water emulsion. Therefore, this chapter will be divided in three sections and each section will discuss the result obtained from each of the above mentioned tasks.

6.1 Determination of the adsorption capacity of organoclay from oil-water emulsion

The study concerning adsorption capacity of the organoclay was accomplished by analyzing data gathered from bucket experiments using various concentrations of oil-water emulsion. As mentioned before, a particular type of oil was used in this research project (SAE 30 oil) to conduct the experiments. This SAE 30 oil has a measured density of 0.72g/ml.

Before this particular research project, several works had been performed to examine the adsorption criteria of the organoclay. Among them, Patel[30] and Furrow[12] are worth mentioning and have great relevance to this research project. Patel[30] found that adsorbent particle size and surface area have a strong affect on the adsorption rate. He also mentioned that adsorption in organoclay media is a two phase process and can be described as the following:

Phase I: Diffusion of oil from the oil-water emulsion to the surface of the organoclay. This phase is driven by mechanical diffusion.

Phase II: The adsorption of oil within the pore structure of the organoclay. This phase is driven by pore diffusion or by surface diffusion.[29]

Furrow[12] determined the effect of oil type on oil adsorption by organoclay. Three different types of oils were used to determine the effect of oil type on oil adsorption by organoclay. It was found that SAE 30 showed best performance as far as the adsorption capacity of the organoclay in the oil water emulsion was concerned. That's why the author decided to use the SAE 30 motor oil in this research project to investigate the adsorption characteristics of the organoclay in the oil water emulsion. The research presented here shows the effect of concentration of oil-water emulsion on oil adsorption in organoclay media. As mentioned many times before, emulsions of 4 different concentrations i.e., 750 ppm, 1000 ppm, 1500 ppm and 2000 ppm oil-water emulsions, were prepared to conduct all the experiments of this research project. Table 1 shows different concentrations of oil/ water emulsions and organoclay loading that have been chosen for the experiments.

Table 1: Experimental bucket specifications

Experimental Bucket Specifications						
Bucket No.	Bucket Concentration (ppm)	Bucket Volume (liters)	Oil Specific Gravity (g/ml)	Oil Weight (grams)	Oil Volume (ml)	Organoclay Weight (gm)
1	750	3	0.72	2.25	3.13	5
2	1000	3	0.72	3.00	4.17	6
3	1500	3	0.72	4.50	6.25	9
4	2000	3	0.72	6.00	8.33	12

6.1.1 Effect of concentration in adsorption media

It is known that if all other parameters are kept constant, adsorption capacity is proportional to concentration of adsorbate in oil water emulsion. Therefore**,** as the concentration of the oil in oil water emulsion increases, an increased amount of oil is also adsorbed in the pore of the organoclay increasing the total adsorption capacity of the adsorbent or organoclay media. This phenomenon was also observed in this research project up to a certain oil concentration level where emulsions were stable. Tables 2, 3 and 4 indicate that for 750 ppm emulsion, the adsorption capacity was found to be 28.20%, for 1000 ppm 35.75% and for 1500 ppm 40.036%. It needs to be mentioned here that, in all of the cases mentioned above, the bucket volume, particle size and the ratio of the oil to organoclay were kept constant. Also the oil-water emulsion was stirred constantly at 1500 rpm to make the emulsion homogeneous.

From the adsorption capacity figures from tables 2, 3 and 4 clearly shows that with the increase in concentration of the oil water emulsion, the adsorption capacity of the organoclay in the oil water emulsion also increased. But a deviation to this trend was observed for the case where the oil water emulsion was 2000 ppm, where the measured capacity was found to be 33.65% as seen in Table 5. In this case instead of getting increased, adsorption capacity actually decreased a little bit. One may wonder why this deviation occurred.

There might be several reasons behind this unexpected behavior of organoclay. It is to be mentioned here that, for data collection, samples were taken at a certain time interval for 750 ppm, 1000 ppm, 1500 ppm and 2000 ppm emulsions. 2000 ppm emulsion is a very concentrated emulsion and therefore it is difficult to obtain stable emulsions out of emulsion of this concentration. As a consequence, oil droplets often coalesce and generate large globules of oil which are difficult to adsorb. Therefore, at 1500 rpm, 2000 ppm emulsion will definitely require more time than other emulsions

(750, 1000 and 1500 ppm emulsions) to become homogeneous. Therefore, it can be concluded that, although 750, 1000 and 1500 ppm emulsions were already homogenous when data were collected from all these emulsions; the 2000 ppm emulsion was yet to be homogeneous and therefore was not eligible for taking data. The author believes that this might have lessened the adsorption efficiency or capacity of the organoclay media in case of highly concentrated 2000 ppm emulsion that was used in the experiments of this research project.

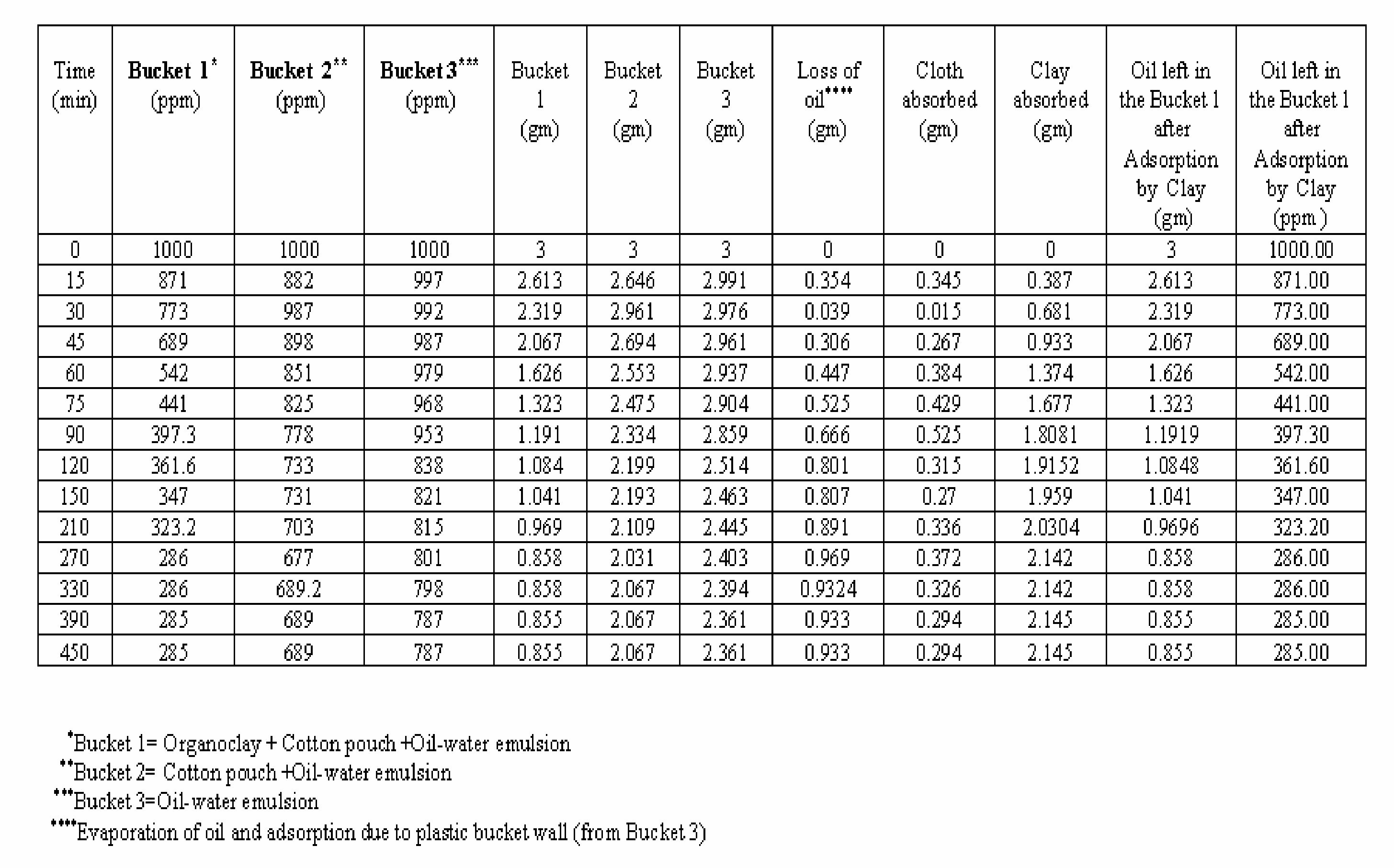
Next four pages show the experimental results for four different concentration emulsions. These results are arranged in tables. The first table shows the experimental results for 750 ppm concentration oil water emulsion. The second one is for 1000 ppm concentration oil water emulsion, while the third and fourth tables for 1500 and 2000 ppm concentration oil water emulsions respectively.

Table 2: Experimental data for 750 ppm oil water- emulsion:

Time (min)	**Bucket 1*** (ppm)	**Bucket 2 **** (ppm)	**Bucket 3***** (ppm)	Bucket 1 (gm)	Bucket 2 (gm)	Bucket 3 (gm)	Loss of oil**** (gm)	Cloth absorbed (gm)	Clay absorbed (gm)	Oil left in the Bucket 1 after Adsorption by Clay (gm)	Oil left in the Bucket 1 after Adsorption by Clay (ppm)
0	750	750	750.00	2.25	2.25	2.25	0.00	0.00	0.00	2.25	750.00
15	725	748	739.00	2.18	2.22	2.24	0.01	0.03	0.04	2.21	736.00
30	716	741	732.00	2.15	2.20	2.22	0.03	0.03	0.05	2.20	734.00
45	698	721.6	715.00	2.09	2.15	2.16	0.09	0.02	0.05	2.20	733.00
60	623	732	689.30	1.87	2.07	2.20	0.05	0.13	0.20	2.05	683.70
75	577	678.03	649.27	1.73	1.95	2.03	0.22	0.09	0.22	2.03	677.73
90	462	634	618.30	1.39	1.85	1.90	0.35	0.05	0.47	1.78	593.70
120	302	598.9	576.00	0.91	1.73	1.80	0.45	0.07	0.82	1.43	476.00
150	266	580.7	552.30	0.80	1.66	1.74	0.51	0.09	0.86	1.39	463.70
210	249	574	548.74	0.75	1.65	1.72	0.53	0.08	0.90	1.35	450.26
270	111	562.15	524.04	0.33	1.57	1.69	0.56	0.11	1.24	1.01	336.96
330	49	521	519.50	0.15	1.56	1.56	0.69	0.00	1.41	0.84	279.50
390	27.5	511.18	500.15	0.08	1.50	1.53	0.72	0.03	1.42	0.83	277.35
450	27.5	512	500.17	0.08	1.50	1.54	0.71	0.04	1.42	0.83	277.33

*Bucket 1= Organoclay + Cotton pouch +Oil-water emulsion
**Bucket 2= Cotton pouch +Oil-water emulsion
***Bucket 3=Oil-water emulsion
****Evaporation of oil and adsorption due to plastic bucket wall (from Bucket 3)

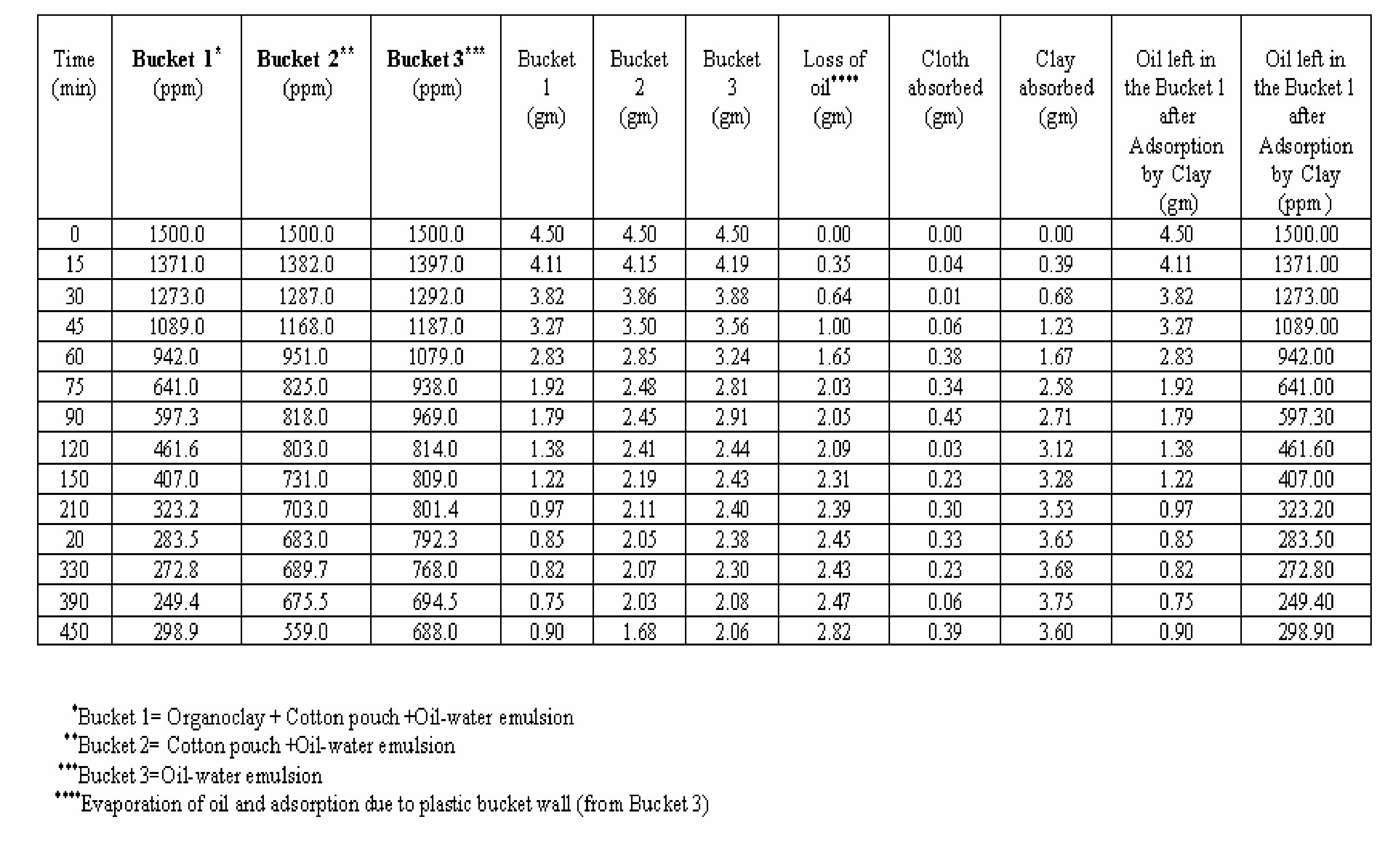
Table 3: Experimental data for 1000 ppm oil water- emulsion:



Time (min)	**Bucket 1*** (ppm)	**Bucket 2**** (ppm)	**Bucket 3***** (ppm)	Bucket 1 (gm)	Bucket 2 (gm)	Bucket 3 (gm)	Loss of oil**** (gm)	Cloth absorbed (gm)	Clay absorbed (gm)	Oil left in the Bucket 1 after Adsorption by Clay (gm)	Oil left in the Bucket 1 after Adsorption by Clay (ppm)
0	1000	1000	1000	3	3	3	0	0	0	3	1000.00
15	871	882	997	2.613	2.646	2.991	0.354	0.345	0.387	2.613	871.00
30	773	987	992	2.319	2.961	2.976	0.039	0.015	0.681	2.319	773.00
45	689	898	987	2.067	2.694	2.961	0.306	0.267	0.933	2.067	689.00
60	542	851	979	1.626	2.553	2.937	0.447	0.384	1.374	1.626	542.00
75	441	825	968	1.323	2.475	2.904	0.525	0.429	1.677	1.323	441.00
90	397.3	778	953	1.191	2.334	2.859	0.666	0.525	1.8081	1.1919	397.30
120	361.6	733	838	1.084	2.199	2.514	0.801	0.315	1.9152	1.0848	361.60
150	347	731	821	1.041	2.193	2.463	0.807	0.27	1.959	1.041	347.00
210	323.2	703	815	0.969	2.109	2.445	0.891	0.336	2.0304	0.9696	323.20
270	286	677	801	0.858	2.031	2.403	0.969	0.372	2.142	0.858	286.00
330	286	689.2	798	0.858	2.067	2.394	0.9324	0.326	2.142	0.858	286.00
390	285	689	787	0.855	2.067	2.361	0.933	0.294	2.145	0.855	285.00
450	285	689	787	0.855	2.067	2.361	0.933	0.294	2.145	0.855	285.00

*Bucket 1= Organoclay + Cotton pouch +Oil-water emulsion
**Bucket 2= Cotton pouch +Oil-water emulsion
***Bucket 3=Oil-water emulsion
****Evaporation of oil and adsorption due to plastic bucket wall (from Bucket 3)

Table 4 : Experimental data for 1500 ppm oil water- emulsion:



Time (min)	**Bucket 1**[*] (ppm)	**Bucket 2**[**] (ppm)	**Bucket 3**[***] (ppm)	Bucket 1 (gm)	Bucket 2 (gm)	Bucket 3 (gm)	Loss of oil[****] (gm)	Cloth absorbed (gm)	Clay absorbed (gm)	Oil left in the Bucket 1 after Adsorption by Clay (gm)	Oil left in the Bucket 1 after Adsorption by Clay (ppm)
0	1500.0	1500.0	1500.0	4.50	4.50	4.50	0.00	0.00	0.00	4.50	1500.00
15	1371.0	1382.0	1397.0	4.11	4.15	4.19	0.35	0.04	0.39	4.11	1371.00
30	1273.0	1287.0	1292.0	3.82	3.86	3.88	0.64	0.01	0.68	3.82	1273.00
45	1089.0	1168.0	1187.0	3.27	3.50	3.56	1.00	0.06	1.23	3.27	1089.00
60	942.0	951.0	1079.0	2.83	2.85	3.24	1.65	0.38	1.67	2.83	942.00
75	641.0	825.0	938.0	1.92	2.48	2.81	2.03	0.34	2.58	1.92	641.00
90	597.3	818.0	969.0	1.79	2.45	2.91	2.05	0.45	2.71	1.79	597.30
120	461.6	803.0	814.0	1.38	2.41	2.44	2.09	0.03	3.12	1.38	461.60
150	407.0	731.0	809.0	1.22	2.19	2.43	2.31	0.23	3.28	1.22	407.00
210	323.2	703.0	801.4	0.97	2.11	2.40	2.39	0.30	3.53	0.97	323.20
20	283.5	683.0	792.3	0.85	2.05	2.38	2.45	0.33	3.65	0.85	283.50
330	272.8	689.7	768.0	0.82	2.07	2.30	2.43	0.23	3.68	0.82	272.80
390	249.4	675.5	694.5	0.75	2.03	2.08	2.47	0.06	3.75	0.75	249.40
450	298.9	559.0	688.0	0.90	1.68	2.06	2.82	0.39	3.60	0.90	298.90

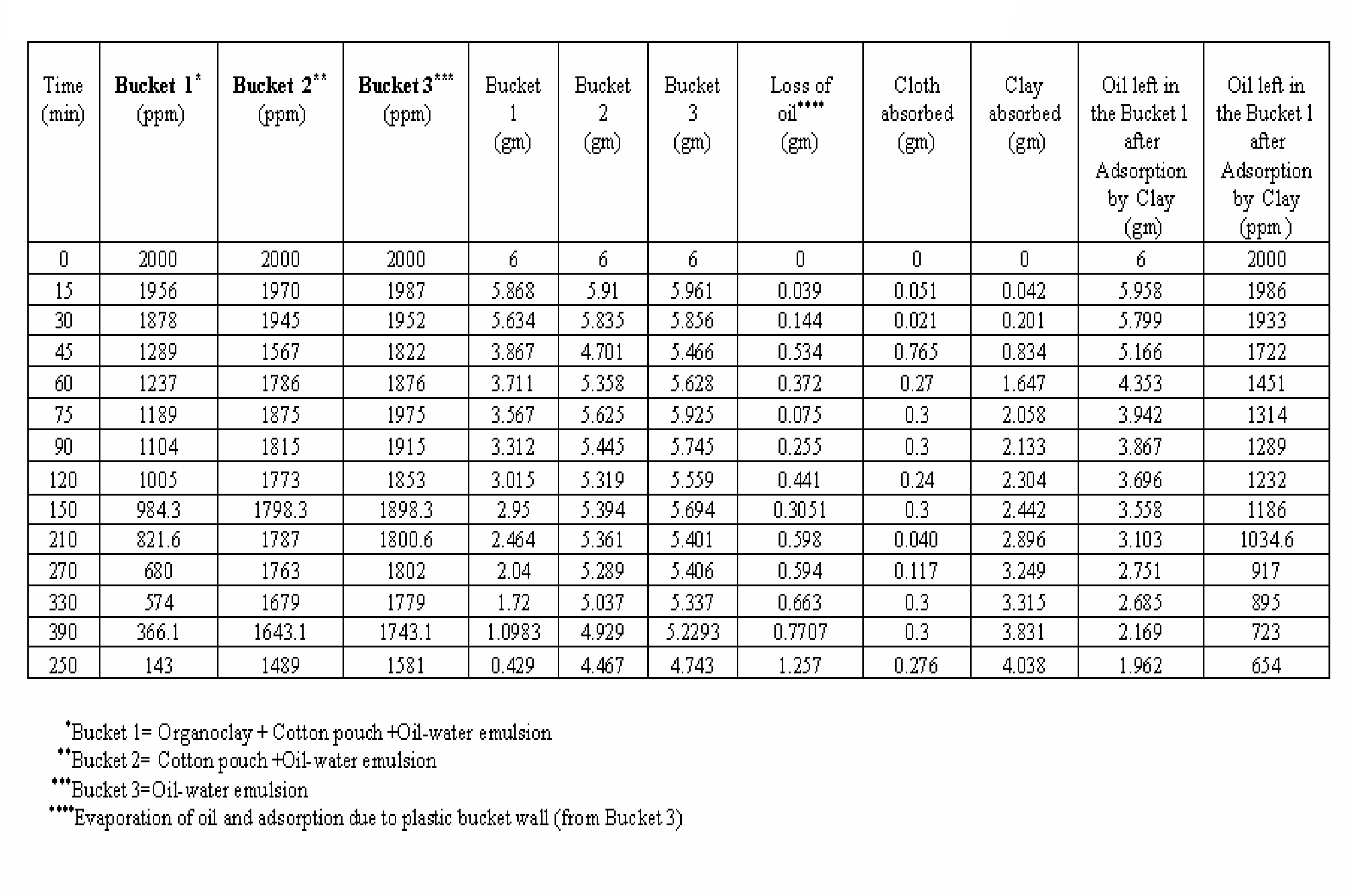
[*] Bucket 1= Organoclay + Cotton pouch +Oil-water emulsion

[**] Bucket 2= Cotton pouch +Oil-water emulsion

[***] Bucket 3=Oil-water emulsion

[****] Evaporation of oil and adsorption due to plastic bucket wall (from Bucket 3)

Table 5 : Experimental data for 2000 ppm oil water- emulsion:



Time (min)	**Bucket 1*** (ppm)	**Bucket 2**** (ppm)	**Bucket 3***** (ppm)	Bucket 1 (gm)	Bucket 2 (gm)	Bucket 3 (gm)	Loss of oil**** (gm)	Cloth absorbed (gm)	Clay absorbed (gm)	Oil left in the Bucket 1 after Adsorption by Clay (gm)	Oil left in the Bucket 1 after Adsorption by Clay (ppm)
0	2000	2000	2000	6	6	6	0	0	0	6	2000
15	1956	1970	1987	5.868	5.91	5.961	0.039	0.051	0.042	5.958	1986
30	1878	1945	1952	5.634	5.835	5.856	0.144	0.021	0.201	5.799	1933
45	1289	1567	1822	3.867	4.701	5.466	0.534	0.765	0.834	5.166	1722
60	1237	1786	1876	3.711	5.358	5.628	0.372	0.27	1.647	4.353	1451
75	1189	1875	1975	3.567	5.625	5.925	0.075	0.3	2.058	3.942	1314
90	1104	1815	1915	3.312	5.445	5.745	0.255	0.3	2.133	3.867	1289
120	1005	1773	1853	3.015	5.319	5.559	0.441	0.24	2.304	3.696	1232
150	984.3	1798.3	1898.3	2.95	5.394	5.694	0.3051	0.3	2.442	3.558	1186
210	821.6	1787	1800.6	2.464	5.361	5.401	0.598	0.040	2.896	3.103	1034.6
270	680	1763	1802	2.04	5.289	5.406	0.594	0.117	3.249	2.751	917
330	574	1679	1779	1.72	5.037	5.337	0.663	0.3	3.315	2.685	895
390	366.1	1643.1	1743.1	1.0983	4.929	5.2293	0.7707	0.3	3.831	2.169	723
250	143	1489	1581	0.429	4.467	4.743	1.257	0.276	4.038	1.962	654

*Bucket 1= Organoclay + Cotton pouch +Oil-water emulsion

**Bucket 2= Cotton pouch +Oil-water emulsion

***Bucket 3=Oil-water emulsion

****Evaporation of oil and adsorption due to plastic bucket wall (from Bucket 3)

6.1.2 Sample calculation

The sample calculation is given below:

Here 750 ppm 3 liter oil- water emulsion is considered.

In 750 ppm 3 liter oil-water emulsion weight of oil $= \frac{C_o \times V}{1000} = \frac{750 \times 3}{1000} = 2.25 gm$

Specific gravity of SAE 30 oil is 0.72gm/ml

So, Volume of oil $= \frac{2.25}{0.72} = 3.125 ml$

Amount of Clay $= 2.25 \times 2 = 4.5 gm$ (ratio of oil: water is 1:2*)*

Now, let us look at the data from the experiments.

After 30 minutes the concentration will change.

Bucket 1: Clay +Cloth =716 ppm (left in the bucket) $= 716 \times \frac{3}{1000} = 2.148$ gm

Bucket2: Cloth = 732 ppm (left in the bucket) $= 732 \times \frac{3}{1000} = 2.196$ gm

Bucket 3: Blank (Evaporation + loss due to plastic bucket) = 741 ppm ((left in the bucket) = $741 \times \frac{3}{1000} = 2.223$ gm

Now, if material balance is conducted,

Amount Evaporated = *2.25 (initial Oil)-2.223=0.027gm*

Amount Absorbed by Cloth = *2.223-2.196=0.027* gm

Total Loss/Adsorption by Cloth + Clay + Evaporation = *2.25-2.148 =0.102* gm

Amount Absorbed only by Clay = *0.102-Evaporation-absor.cloth*

$$= 0.102-0.027-0.027$$

$$= 0.048 \ gm$$

Therefore, Oil left in the bucket after Adsorption by clay = $2.25-0.048$

$$= 2.202gm$$

Ratio of initial concentration and concentration at a certain time interval,

$$C_0 = 2.202\times\frac{3}{1000} = 734 \ ppm$$

$$\frac{C_0}{C_i}=\frac{734}{750} = 0.98$$

6.2 Adsorption isotherm model

The adsorbability of organoclay or the relative affinity of organoclay for oil can be determined by using an adsorption isotherm model. The most commonly used isotherm models are Langmuir, BET (Brunauer, Emmet and Teller) and Freundlich isotherm models. These methods are generally used for developing environmental models, explaining experimental adsorption data, characterizing surfaces and designing pollution control equipment.[25] The Langmuir isotherm considered as a physisorption of gases or liquid solutes on solids when only a monolayer of adsorbate is formed. This is considered to be a prime limitation of the Langmuir isotherm model, since it is well known that during the physisorption process, multiple layers of adsorbate can be formed. The BET isotherm model eliminates the limitation that arises in the Langmuir isotherm and envisages the formation of a multilayer of adsorbate. The BET model assumes that individual layers need not be complete and that the Langmuir model applies to adsorption in each layer, although the interaction of the first layer with the adsorbate surface can have a different heat of adsorption (adsorption enthalpy) than that between successive layers. The BET adsorption is best applicable for gas adsorption studies.[29]

The Freundlich isotherm is typically used as an empirical adsorption model for solid-liquid systems. Since oil-water emulsion in organoclay media is a solid-liquid system and since that is the kind of system that was used in this research project, the Freundlich isotherm model was used to establish the kinetic model of organoclay used in this research project. The model was used to fit data rather than to verify an adsorption mechanism.[25,29]

6.2.1 Data generation for adsorption isotherm

The data generated from an adsorption isotherm depends on the measurement of residual adsorbate remaining in the emulsion. This concentration can be measured directly or it may be measured as a gross value, for example, Total Organic Carbon (TOC) or UV absorbance. In this experiment UV absorbance, or the fluorescence technique, was adopted to measure the residual concentration of the experimented emulsion. In conducting the test, organoclay dosage was applied to various concentrations of oil /water emulsion. As mentioned in section 5.3, the weight ratios of organoclay to oil were kept constant at 2:1. The values of the organoclay dosage are recorded and were designated as m. Then the amount of oil adsorbed (gm) in organoclay was measured and was designated as x. After these values were obtained, the organoclay capacity was calculated as '*x/m*' (gm/gm). Also, the equilibrium concentration for each type of 4 different oil-water emulsions, *Ce,* (ppm), was obtained from concentration vs. time plot Fig. 9. The isotherm data was then plotted on a logarithmic graph as 'x/m' on the ordinate versus 'C_e' on the abscissa as shown in Fig. 8. After plotting the data points, the graphical relationship between the adsorption capacity (*x/m*) and the equilibrium concentration (C_e) was obtained. Table 6 below shows the data for isotherm calculation.

Table 6: Data for isotherm calculation

Concentration of the emulsion (ppm)	Equilibrium Concentration C_e (ppm)	Amount of adsorbate adsorbed per gm of adsorbent q_e (gm/gm)
750	277.33	0.2836
1000	285	0.3575
1500	298.9	0.4003
2000	654	0.5639

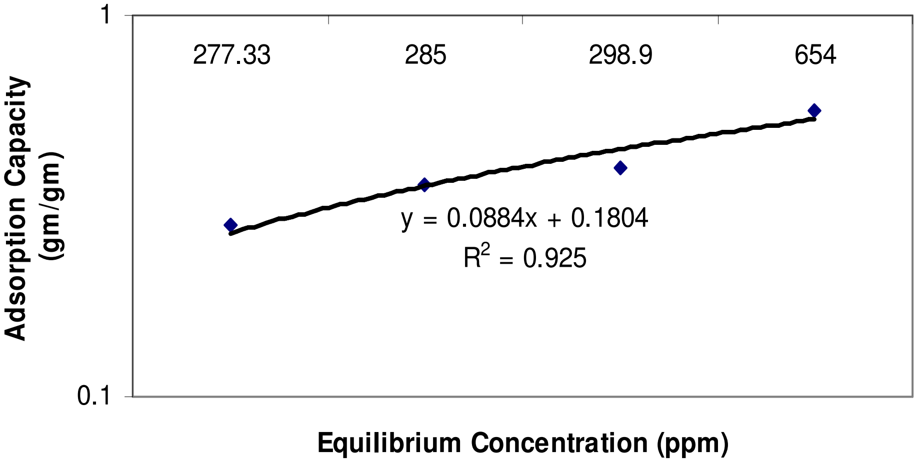


Fig. 8- Adsorption isotherm model

From Fig. 8, adsorption parameter from slope n=1/.0884 =11.3 and from intercept K_f= 1.514 (gm/gm) (L/gm)$^{1/n}$

Here K_f is an empirical constant related to the capacity of the adsorbent material to adsorb the adsorbate and n is a constant related to the affinity of the adsorbate for the surface.

6.2.2 Interpretation of adsorption isotherm

A great deal of very important information can be obtained from proper evaluation of the data generated from the adsorption isotherm.

6.2.2.1 Isotherm slope

Useful information can be obtained by inspecting the slope of the isotherm plot. The slope can be shallow or steep. If the slope is shallow, it can be concluded that the adsorbate removal per weight of the adsorbent is nearly equal at all equilibrium concentrations along the isotherm plot. This adsorbate (oil) shows the high affinity for the adsorbent (organoclay) independent of equilibrium concentration. From the practical standpoint, this type of system could be treated in the batch process.[25] The adsorption isotherm graph plotted with readings from this research falls in this shallow slope category.

Steep isotherms indicate that the adsorption capacity is highly dependent on equilibrium concentration. If a batch system is utilized, adsorbent dosages required in this case would increase markedly for a very small reduction in residual concentrations. So a batch system is not usually suitable for this particular category of isotherm.

6.2.2.2 Adsorption usage rate

Adsorption isotherm can be viewed as a relationship between adsorbent capacity and equilibrium concentration on an equilibrium batch system. This data can be employed to make a prediction regarding the adsorbent dosage (i.e., rate of usage) for a fixed column type system.[25] The fixed bed adsorber can be considered to be an infinite number of series of batch adsorption stages, each of which comes to equilibrium at different concentrations. Across the bed, one can have concentrations ranging from C_o (maximum concentration of the isotherm) to zero (minimum concentration of the isotherm) and corresponding x/m values. It is impossible to realistically explain the capacity throughout the column using either $(x/m)C_o$ value or the effluent concentration objective x/m value. But it is possible to realize some intermediate values that exist between these points. From these two values, one can obtain the maximum and minimum usage rate of carbon (or organoclay for this research project). Thus the use of these maximum and minimum values of the organoclay usage rate can allow someone to determine the range of cost associated with the operating system[25].

A simple example from this research project will clarify this dosage issue. With reference to the Fig. 8, it can be seen that when equilibrium concentration is 0 (zero) ppm, the corresponding x/m value is 0.1804 gm/gm. This is the minimum value. Now, when the concentration value is 654 ppm, the corresponding x/m value is 0.5639 gm/gm.

This is the maximum value. The use of these two *x/m* values or usage rate or adsorption capacity of organoclay by the process engineer will allow bracketing of carbon or organoclay usage rate and therefore the cost of an operating system.

6.2.2.3 Single or similar adsorbates

If a single component system is used, a straight line pattern is supposed to be obtained from a concentration versus adsorption capacity plot. Moreover this straight line plot should abide Freundlich equation independent of whether gross or specific analytical methods are used. Sometimes, a fluid can contain multiple components that may have similar adsorption potential. This means that, those components will also have similar values of adsorption parameters K_f and n. In that case, the adsorption plot for such a fluid would be linear and would resemble a single component system.[25, 29]

6.3 Kinetics of the organoclay adsorption media

Kinetics of the organoclay media can be determined by plotting concentration of oil-water emulsion over a certain time interval. Fig. 9 shows the dynamic pattern for various concentrated oil-water emulsion in organoclay media and Fig. 10 shows the same dynamic pattern but using a dimensionless concentrations (C_o/C_i).

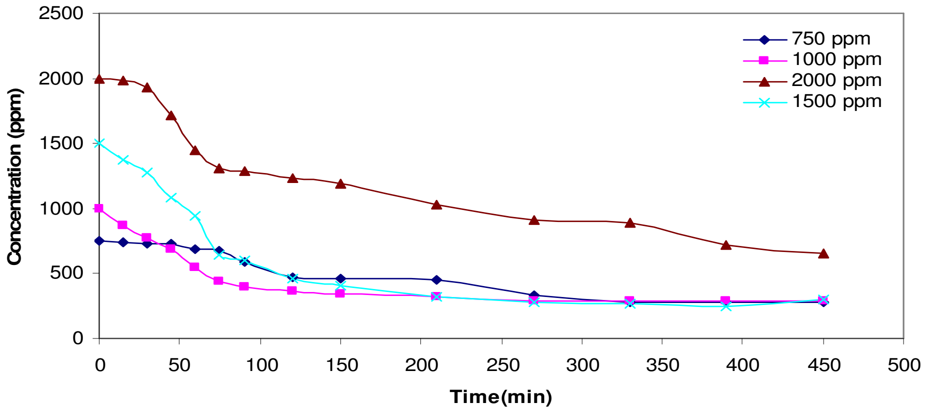


Fig. 9 - Concentration profile with experimental data

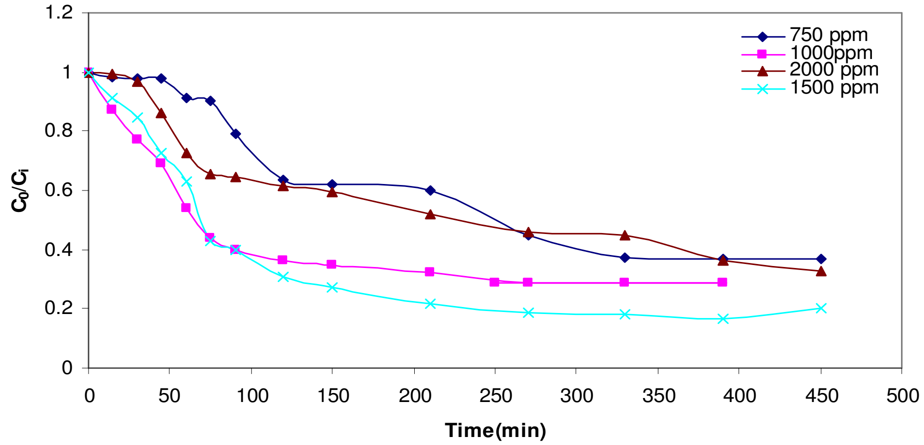


Fig. 10 - Dimensionless concentration profile with experimental data.

6.4 Oil loading capacity versus kinetics

From the experimental data and graphs it can be seen that capacity parameters determine the loading characteristics of granular organoclay media. The maximum oil adsorption capacity of organoclay is only achieved at equilibrium and it can be estimated from concentration vs. time plot. Kinetic parameters only determine the rate of adsorption and are independent of the adsorption capacity of the organoclay media.

6.5 Kinetic pattern of organoclay using adsorption parameters K_f and n

A kinetic pattern of the organoclay was developed using the adsorption parameters K_f and n in a MATLAB programming (Appendix). The reader may remember that these adsorption parameters K_f and n were obtained from Freundlich Isotherm Model which was discussed in section 6.2. As the reader may notice, this MATLAB programming is arranged in a loop. It was assumed that after every step, the adsorption process had reached its equilibrium. The plot in Fig. 11 was obtained using this above mentioned program for 1000 ppm oil-water emulsion concentration. It is to be mentioned here that the concentration data in the Fig. 11 was plotted as the gm oil present in the 1000 ppm oil-water emulsion. Although MATLAB was used to write the code for this kinetic model, it is to be mentioned here that any standard coding language can be used to achieve this program using the following step by step methodology:

At time, $t = 0$, Concentration, $C = C_0$

and at $t = 1$, Concentration, $C = C_1$

Therefore, at time, $t = i\text{-}1, C = C_{i-1}$

and $t = i$, $C = C_i$

Here, $C_i < C_{i-1}$

Now, from Freundlich isotherm that deals with equilibrium concentration,

$$q = K_f C_i^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(12)}$$

Where $q = \dfrac{\textit{amount of oil adsorbed by clay}}{\textit{Total amount of clay}} = \dfrac{W_{ads}}{m}$ *(gm/gm)* ... ……………………(13)

Therefore, from Equation (12) and (13) above,

$$W_{ads} = m(K_f C_i^{1/n}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(14)}$$

Therefore, it can be deduced that,

$C_i = C_{i-1}$ – *amount of oil adsorbed by the organoclay*

$= C_{i-1} - W_{ads}$

$= C_{i-1} - m\ (K_f\ C_i^{\ 1/n}$ …………………………………………………..(15)

It is to be mentioned here that the units for C_i, m, K_f, n were converted to weight basis and the time unit was taken as minute. The reason behind taking minute as the time unit was because all the experimental data were also recorded by taking minute as a time unit. That's why minute was also considered as a time unit for this model. Now, a graphical relation between the concentration and time step were plotted and Fig. 11 was obtained. It is important to mention that total time for this plot was taken to be 360 minute. That means, concentration profile was obtained for 360 minutes by using the Equation (15) mentioned above and was plotted against time in Fig. 11.

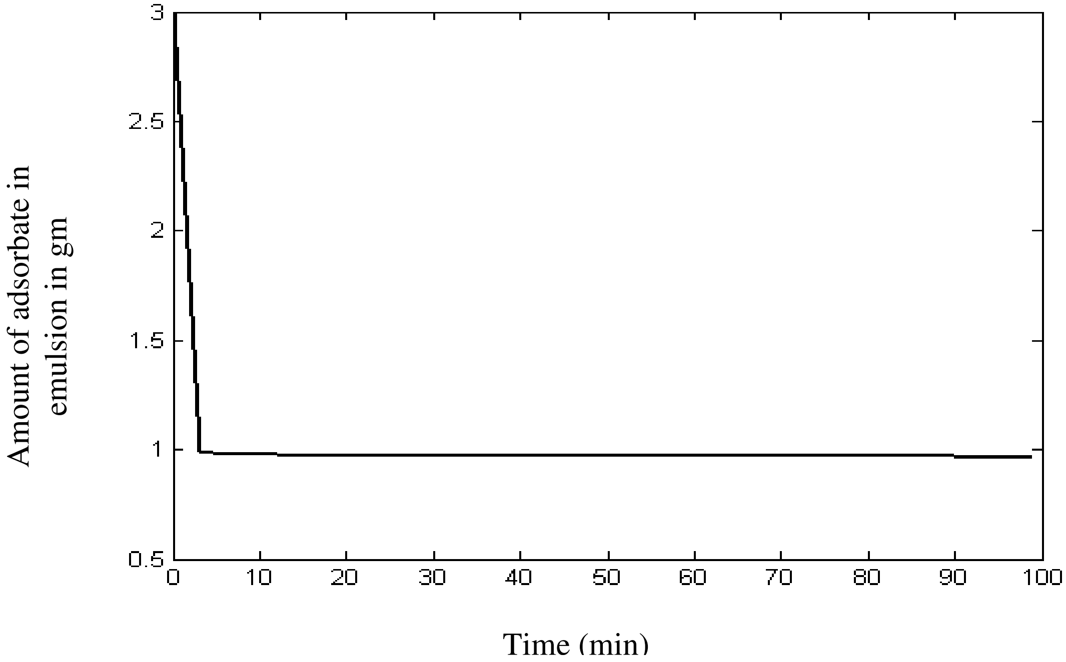


Fig. 11 - Concentration profile using K_f and n.

But later it was found that this method had a serious shortcoming. The Freundlich Isotherm Model is explicitly for equilibrium conditions. But there was no guarantee that equilibrium condition was attained after each time step in the previously described methodology. Actually this was an assumption made for this program which was not even valid as far as practical condition concerning organoclay in oil water emulsion was concerned. Moreover, the time variable used in this programming had no definite unit and that made the process independent of time which was not desired at all. Because kinetic behavior must show dependence on time, it can be concluded that this methodology of developing kinetic model using adsorption parameters was not applicable if one wanted to examine kinetic behavior of organoclay.

One other important shortcoming of this model can be demonstrated by the results shown in the Fig. 11. It can be seen from the figure that change of amount of oil adsorbed by the organoclay in the oil water emulsion was very drastic and occurred only within the first 10 minutes. After this first 10 minutes period, the change of this amount of oil is almost flat. And one may see that this causes the slope of the graph to be very steep. But in practice, this trend of change of amount of oil adsorbed by the organoclay in the oil water emulsion was rather gentle or smooth as can be found in Fig. 9. Moreover, in actual case, this change of amount of oil occurred throughout the length of the experiment (i.e., almost 1.5 hour), not only within the first 10 minutes of the experiment. Therefore, it can easily be said that this model, by no means, can represent the actual kinetic behavior of the organoclay in the oil water emulsion.

Therefore, a different approach was needed to develop a kinetic model for organoclay. To follow is a brief description of the methodology of the newly developed kinetic model of organoclay along with the results obtained from it.

6.6 Kinetic model development

It was necessary to verify whether experimental results followed any established kinetic adsorption model. To do this, the author wanted to verify the experimental results with respect to the kinetic model proposed by Vermuelen and Heister. [31,,32] According to this model, the rate of solute adsorption is a first order kinetics and was assumed governed by the following equation:

$$\frac{d(C-C_e)}{dt} = k_r(C-C_e) \quad \text{...} \quad (16)$$

Where C = Concentration of solute (oil) in liquid phase (oil water emulsion) at time't'. This is actually obtained from bucket experiments. (ppm)

C_e = Equilibrium Concentration of solute (oil). Value of C_e can be obtained from Table 3, Table 4and Table 5. (ppm)

k_r = Rate parameter which accounts for the diffusive transport of the solid through a quiescent liquid layer surrounding each solid particles (1/time)

Now, considering the following boundary conditions,

When $t = 0, C = C_o$

$t = \alpha, C = C_e$

Integrating and using these boundary conditions in equation (16),

$$C = (C_0 - C_e)e^{-k_r t} + C_e \quad \text{...} \quad (17)$$

After linearizing and rearranging equation (17), one gets the following,

$$ln(C - C_e) = ln(C_0 - C_e) - k_r t \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (18)$$

Considering various experimental values of C, Table 7 was prepared for the sample of concentration 750 ppm. The value of C_0 in this case is obviously 750 ppm. Then a graphical relation between $ln(C-C_e)$ and time t was plotted as shown in Fig. 12. The slope of the trend line of this plot is k_r of Equation (18). Now, if this value of k_r is used in Equation (17), a new value of concentration is obtained. This concentration value represents the concentration of oil water emulsion proposed by the Vermuelen and Heister model and therefore will be referred to as $C_{predicted}$. The last column of Table 7 shows various $C_{predicted}$ values corresponding to the experimentally obtained values of C. Now, if a graph is plotted for C and $C_{predicted}$ against time variable, it will be possible to examine how closely the experimental values of C follow the established kinetic model. Fig. 13 shows the comparison graphically. It can be seen that the concentration values obtained through experiments very closely follow the established kinetic model.

Similar procedures were followed for 1000 ppm, 1500 ppm and 2000 ppm oil water emulsions and the results are provided in Table 8, Table 9 and Table 10 and also in Fig. 14, Fig. 15, Fig. 16, Fig. 17, Fig. 18 and Fig. 19.

Table 7: Data for model development for a 750 ppm emulsion

Experimental Concentration C (ppm)	C-Ce (ppm)	ln(C-Ce)	Time (min)	*$C_{predicted}$ (ppm)*
750	472.67	6.158397	0	750.00
736	458.67	6.128331	15	677.50
734	456.67	6.123961	30	616.13
733	455.67	6.121769	45	564.16
683.7	406.37	6.007264	60	520.17
677.73	400.4	5.992464	75	482.92
593.7	316.37	5.756912	90	451.39
476	198.67	5.291645	120	402.09
463.7	186.37	5.227734	150	366.75
450.26	172.93	5.152887	210	323.27
336.96	59.63	4.088159	270	300.93
279.5	2.17	0.774727	330	289.46
277.35	0.02	0.9416	390	283.56

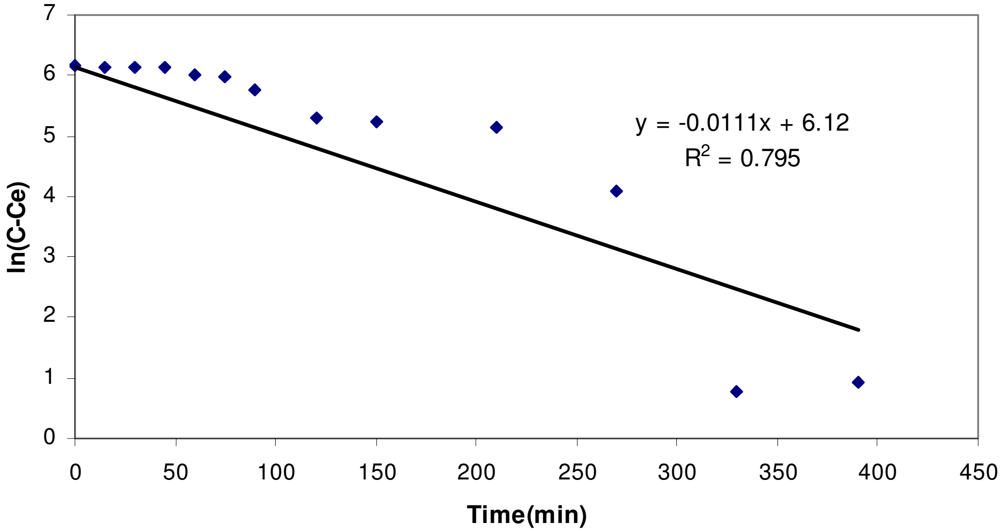


Fig. 12 – Graphical representation of ln(C-C_e) vs. time t plotted to determine the rate parameter k_r for a 750 ppm oil-water emulsion

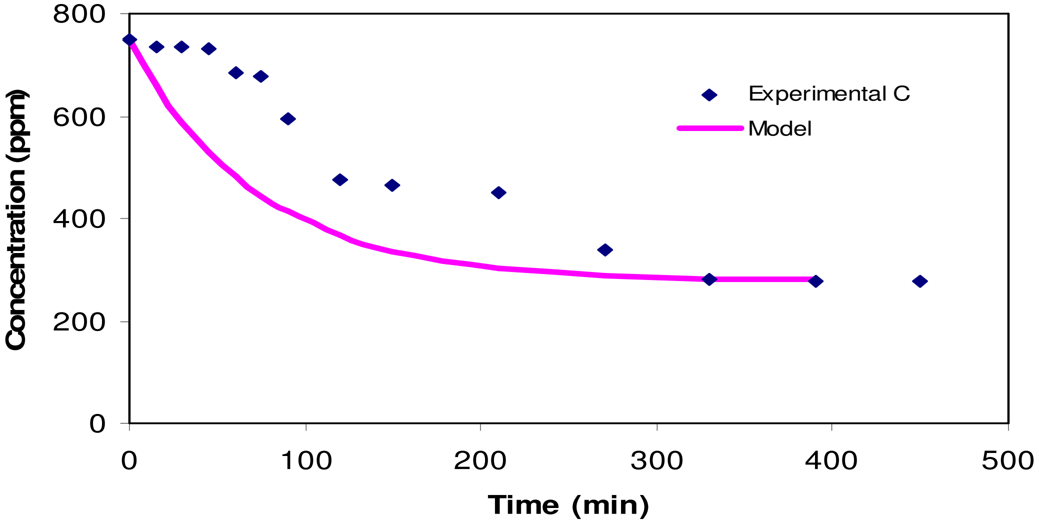


Fig. 13 – Graphical comparison between experimental and model kinetic behaviors for a 750 ppm oil-water emulsion

Table 8: Data for model development for a 1000 ppm emulsion

Experimental Concentration C (ppm)	C-Ce (ppm)	ln(C-Ce)	Time (min)	$C_{predicted}$ (ppm)
1000	715	6.572283	0	1000
871	586	6.37332	15	808.367
773	488	6.190315	30	668.095
689	404	6.001415	45	565.418
542	257	5.549076	60	490.261
441	156	5.049856	75	435.247
397.3	112.3	4.721174	90	394.978
361.6	76.6	4.338597	120	343.926
347	62	4.127134	150	316.572
323.2	38.2	3.642836	210	294.064
286	1	0	270	287.602
286	1	0	330	285.747

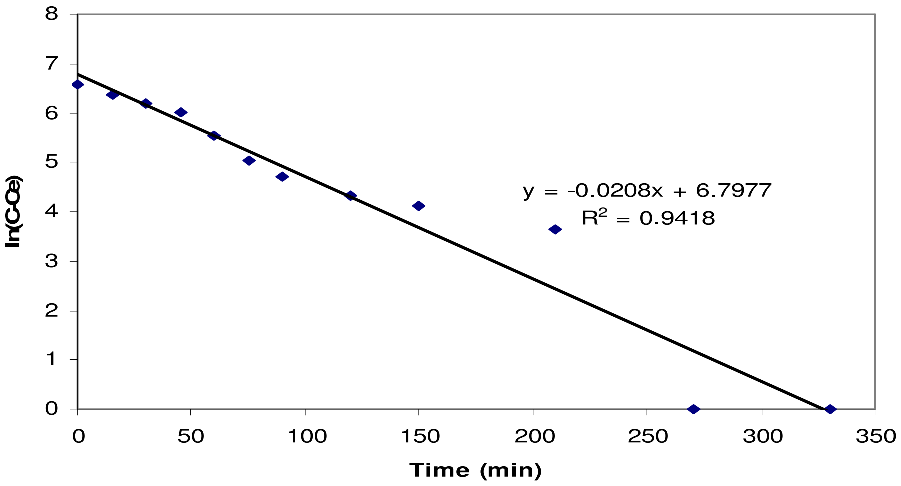


Fig. 14- Graphical representation of ln(C-C_e) vs. time t plotted to determine the rate parameter k_r for a 1000 ppm oil-water emulsion

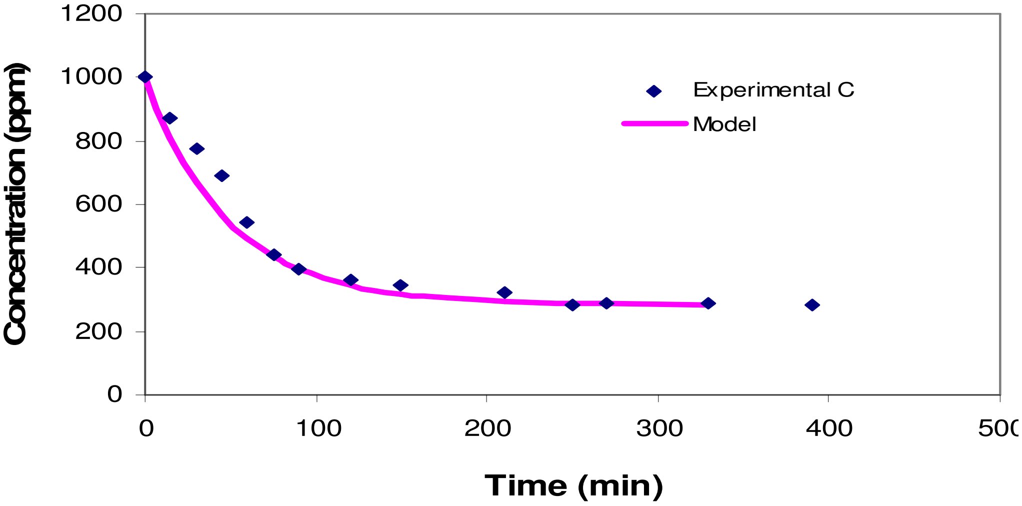


Fig. 15- Graphical comparison between experimental and model kinetic behaviors for a 1000 ppm oil-water emulsion

Table 9: Data for model development for a 1500 ppm emulsion

Experimental Concentration C (ppm)	C-Ce (ppm)	ln(C-Ce)	Time (min)	$C_{predicted}$ (ppm)
1500	1201.1	7.091	0	1500.00
1371	1072.1	6.977	15	1149.54
1273	974.1	6.882	30	901.34
1089	790.1	6.672	45	725.56
942	643.1	6.466	60	601.07
641	342.1	5.835	75	512.90
597.3	298.4	5.698	90	450.46
461.6	162.7	5.092	120	374.92
407	108.1	4.683	150	337.03
323.2	24.3	3.190	210	308.49
302.5	3.6	1.281	270	301.31
301	2.1	0.742	330	299.51
299	0.1	-2.303	390	299.05

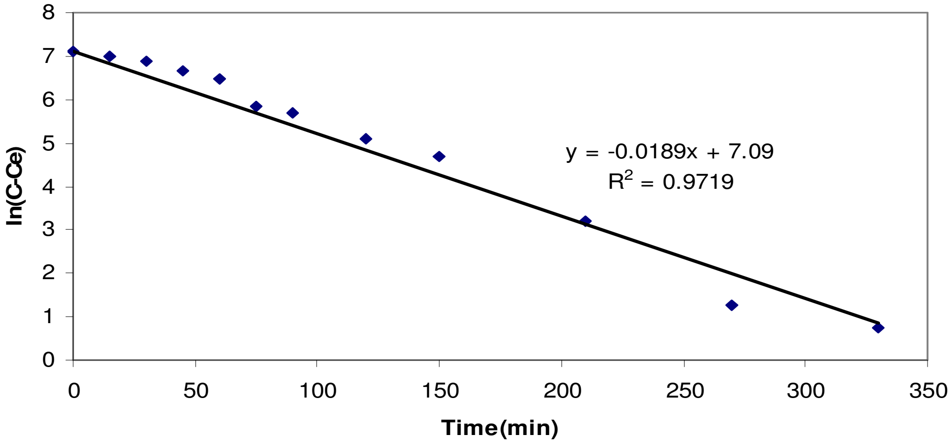


Fig 16- Graphical representation of ln(C-C_e) vs. time t plotted to determine the rate parameter k_r for a 1500 ppm oil-water emulsion

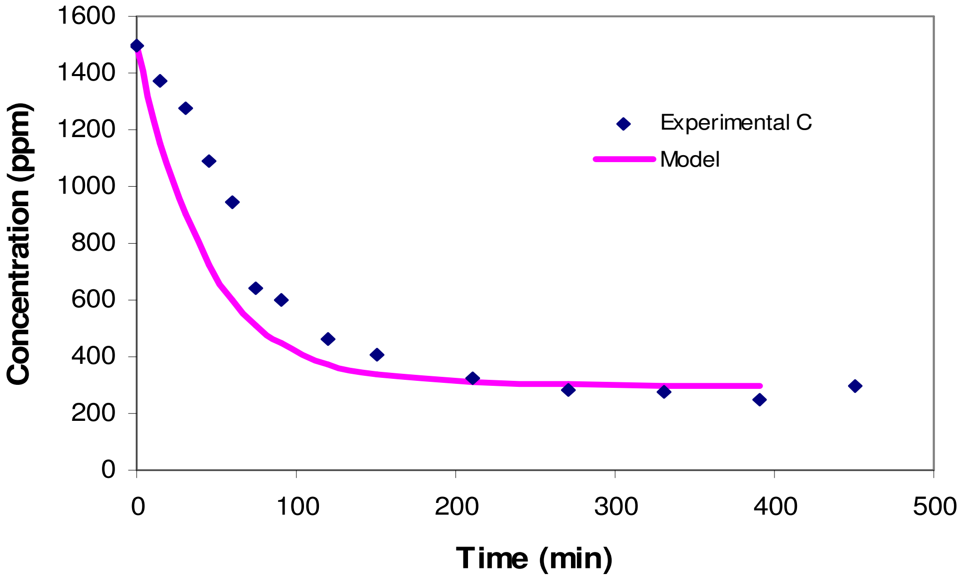


Fig. 17- Graphical comparison between experimental and model kinetic behaviors for a 1500 ppm oil-water emulsion

Table 10: Data for model development for a 2000 ppm emulsion

Experimental Concentration C (ppm)	C-Ce (ppm)	ln(C-Ce)	Time (min)	$C_{predicted}$ (ppm)
2000	1346	7.204893	0	2000.00
1986	1332	7.194437	15	1874.96
1933	1279	7.153834	30	1761.54
1722	1068	6.973543	45	1658.65
1451	797	6.680855	60	1565.32
1314	660	6.49224	75	1480.66
1289	635	6.453625	90	1403.86
1232	578	6.359574	120	1271.01
1186	532	6.276643	150	1161.70
1034.6	380.6	5.941749	210	997.74
917	263	5.572154	270	886.73
895	241	5.484797	330	811.57
723	69	4.234107	390	760.69

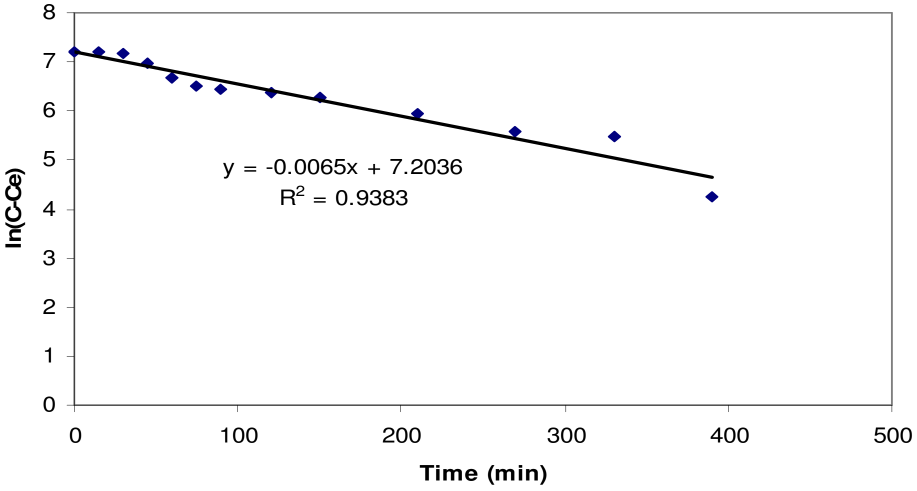


Fig. 18- Graphical representation of ln(C-C_e) vs. time t plotted to determine the rate parameter k_r for a 2000 ppm oil-water emulsion

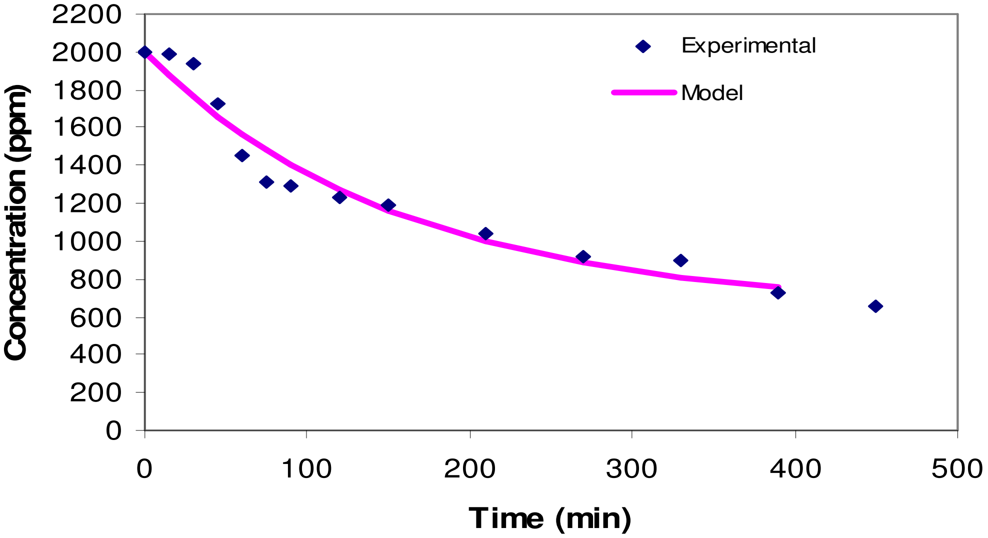


Fig. 19- Graphical comparison between experimental and model kinetic behaviors for a 2000 ppm oil-water emulsion

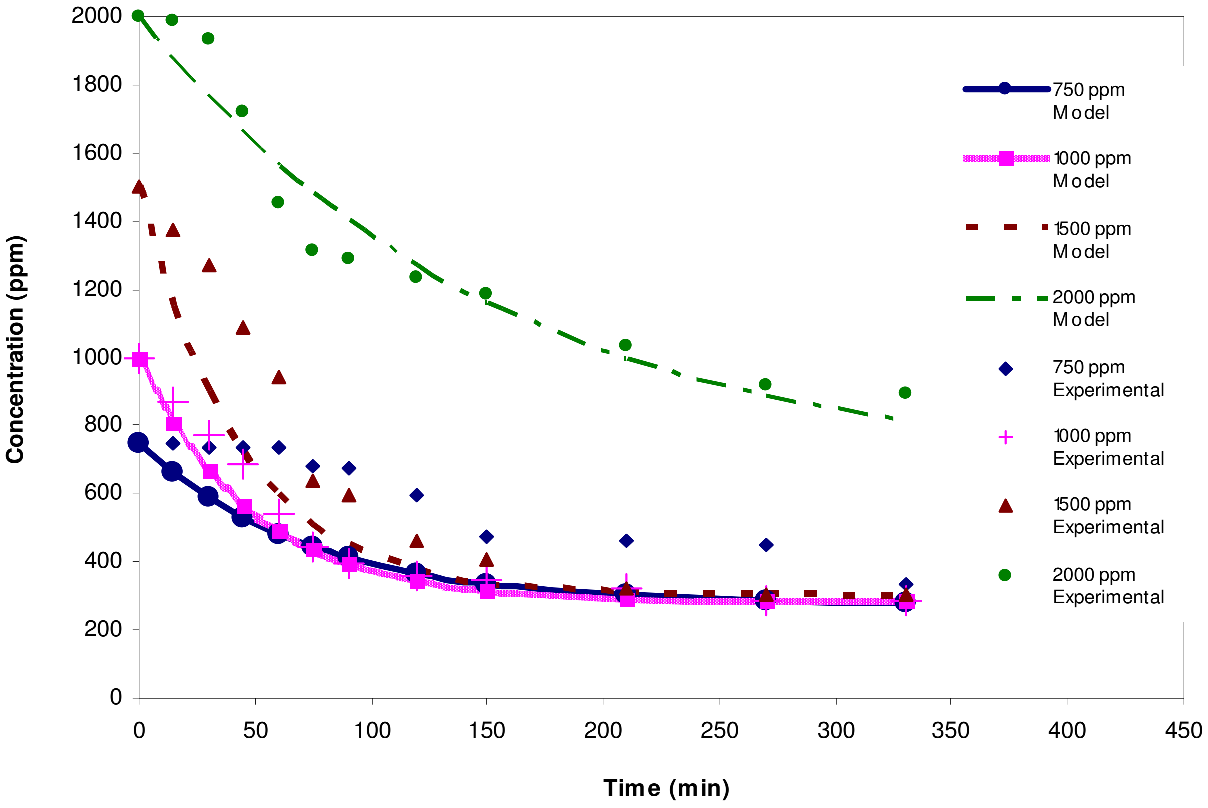


Fig. 20- Graphical representation of experimental and model kinetic behaviors for 750, 1000, 1500 and 2000 ppm oil-water emulsion

Thus Figs. 16, 17, 18 and 19 represent the graphical comparison between the experimental and model kinetic profile for 750 1000 1500 and 2000 ppm emulsions respectively. To present the whole scenario, the author has arranged all these profiles in Fig. 20 so that the reader can have an overview of how closely the experimental results match the proposed model as far as the kinetic profile of the adsorption of organoclay in SAE 30 oil water emulsion is concerned. It can be seen that, although for most part the experimental results do match the proposed model for kinetic profile of the adsorption of organoclay in oil water emulsions, for 750 and 1500 ppm, the experimental results seem to be a little bit deviated from the first order kinetic model proposed by the Vermulen and Heister.[31]Although the deviation is not too significant, it is author's belief that a better correlation between the experimental results and the kinetic model data can be achieved. To accomplish this, it is the author's belief that the kinetic model should be made dimensionless so that it does not depend on the order of the kinetics. Such a model is developed and is discussed in the next section.

6.7 Development of dimensionless kinetic model

The model developed in section 6.6 was a first order kinetic model proposed by Vermulen and Heister.[31] Four separate profiles of concentration vs. time were obtained for four different concentrations of the oil water emulsion to compare the experimental results with those obtained from the model. It was found that, although, for most part, the model seemed to agree with the experimental results, for some part, experimental results don't match very closely to the proposed model. The reason behind this disagreement between the experimental and model data may be attributed to the fact that the adsorption kinetics of organoclay, which was used in this research project, did not follow first order kinetics. As was mentioned in section 6.6, Vermulen and Heister model is a first order kinetic sorption model.[31] Therefore, for the experimental results to match the model; the organoclay must also follow first order adsorption kinetics. Since, for some part, the experimental results did not follow the Vermulen and Heister model closely, it can be concluded that, during the experimental procedure, may be the adsorption kinetics of the organoclay used for the system was not following first order kinetics.

Moreover, in the previous model, four different values of k_r or kinetic parameters were obtained for four different concentrations of oil water emulsion. Using these four different values, four different kinetic patterns were achieved for four different concentrations. But it is always better to have a single value of k_r or kinetic parameter irrespective of the concentration of the oil water emulsion. If that were done, all the model values (irrespective of concentration of oil water emulsion) could have been put together in a single kinetic pattern and a better idea of the kinetic behavior of the organoclay could be attained. For all these reasons, a dimensionless kinetic model was developed to obtain a better comparison between the experimental results and the model values.

Following is a brief description of the development of the dimensionless kinetic model for the adsorption of organoclay in the oil water emulsion. In this model, a dimensionless concentration parameter θ and a dimensionless time parameter Γ were introduced and a relation between θ and Γ was developed by using the reaction order (referred to as n) and reaction kinetic (referred to as k_θ) which were determined from least square method.

First, let us define the dimensionless concentration parameter, θ,

$$\theta = \frac{C - C_e}{C_0 - C_e} \quad \text{………………………………………………………………………..} \quad (19)$$

Where, C = Concentration of the oil water emulsion at time t (ppm)

C_e = Concentration of the oil water emulsion at equilibrium (ppm)

C_o = Initial concentration of the oil water emulsion (ppm)

Boundary Conditions:

When $t = t_o$ $C=C_0$ $\theta =1$
$t = t_e$ $C= C_e$ $\theta =0$

Now, let us define the dimensionless time parameter, Γ,

$$\Gamma = \frac{t_e - t}{t_e - t_0} \quad \text{…………………………………………………………………………} \quad (20)$$

Where, t_e = Time for the oil water emulsion to reach equilibrium (min)

t_o = Initial time for oil water emulsion (min)

Boundary Conditions:

When, $t = t_e$ $\Gamma = 0$
$t= t_o$ $\Gamma = 1$

Now, the reaction kinetics can be expressed as

$$\frac{dC}{dt} = k_r C^n \quad \text{………………………………………………………………………} \quad (21)$$

Where, C = Concentration at time t (ppm)

k_r = Reaction rate constant (1/time)

n = Order of the reaction

Having introduced the dimensionless concentration and time parameters, θ and Γ, Equation (21) can be expressed as the following:

$$\frac{d\theta}{d\Gamma} = k_\theta \theta^n \quad \text{……………} \quad (22)$$

Where, k_θ = Reaction rate constant in dimensionless form

Integrating,

$$\frac{\theta^{(1-n)}}{(1-n)} = k_\theta \Gamma \quad \text{……………} \quad (23)$$

$$\theta^{(1-n)} = k_\theta \Gamma (1-n) \quad \text{……………} \quad (24)$$

Taking logarithm on both side and rearranging,

$$(1-n)\ln\theta = \ln[k_\theta \Gamma(1-n)] = \ln k_\theta + \ln[\Gamma(1-n)]$$

$$(1-n)\ln\theta = \ln\left[k_\theta(1-n)\right] + \ln\Gamma$$

$$\ln\theta = \frac{\ln\left[k_\theta(1-n)\right]}{(1-n)} + \frac{\ln\Gamma}{(1-n)} \quad \text{……………} \quad (25)$$

If ln θ and $\ln\Gamma$ are plotted, one can obtain $\frac{1}{1-n}$ as the slope and $\frac{\ln\left[k_\theta(1-n)\right]}{(1-n)}$ as the intercept. The table in the next page shows various values of θ_{exp}, ln θ and $\ln\Gamma$ obtained for different time.

Table 11: Data for determining kinetic parameters for dimensionless kinetic model development of 750, 1000 and 1500 ppm emulsion.

Time t (min)	θ_{exp}	Γ	$\ln\theta$	$\ln\Gamma$
0	1	1.0000	0	0
15	0.970381	0.9545	-0.03007	-0.04652
30	0.96615	0.9091	-0.03444	-0.09531
45	0.964034	0.8636	-0.03663	-0.1466
60	0.859733	0.8182	-0.15113	-0.20067
75	0.847103	0.7727	-0.16593	-0.25783
90	0.669325	0.7273	-0.40149	-0.31845
120	0.420314	0.6364	-0.86675	-0.45199
150	0.394292	0.5455	-0.93066	-0.60614
210	0.365858	0.3636	-1.00551	-1.0116
270	0.126156	0.1818	-2.07024	-1.70475
0	1	0.954545	0	-0.04652
15	0.81958	0.886364	-0.19896	-0.12063
30	0.682517	0.818182	-0.38197	-0.20067
45	0.565035	0.75	-0.57087	-0.28768
60	0.359441	0.681818	-1.02321	-0.38299
75	0.218182	0.613636	-1.52243	-0.48835
90	0.157063	0.545455	-1.85111	-0.60614
120	0.107133	0.409091	-2.23369	-0.89382
150	0.086713	0.272727	-2.44515	-1.29928
0	1	1	0	0
15	0.892598	0.944444	-0.11362	-0.05716
30	0.811007	0.888889	-0.20948	-0.11778
45	0.657814	0.833333	-0.41883	-0.18232
60	0.535426	0.777778	-0.62469	-0.25131
75	0.284822	0.722222	-1.25589	-0.32542
90	0.248439	0.666667	-1.39256	-0.40547
120	0.135459	0.555556	-1.99909	-0.58779
150	0.090001	0.444444	-2.40794	-0.81093
210	0.020231	0.222222	-3.90052	-1.50408

Using the values of $\ln \theta$ and $\ln \Gamma$, kinetic parameter k_θ and order of the reaction n were obtained from least square analysis.

In the next step, this k_θ value was plugged into the Equation (21). This plugging of the k_θ value facilitated the author to obtain θ values from dimensionless model. It is to be mentioned here that these θ values were actually predicted values and that's why they were referred to as $\theta_{\text{predicted.}}$ However, the experimental values of θ were obtained from Equation (19) and were referred to as θ_{expt}. All these values of $\theta_{\text{predicted}}$ and θ_{expt} are shown in Table 12. It is to be noted that these $\theta_{\text{predicted}}$ and θ_{expt} are recorded in Table 12 with respect to time, t and dimensionless time parameter Γ.

Table 12: Data for dimensionless kinetic model development for 750, 1000 and 1500 ppm emulsion.

Time t (min)	θ_{exp}	Γ	$\theta_{predicted}$
0	1	1.0000	1.085111
15	0.970381	0.9545	0.974029
30	0.96615	0.9091	0.869722
45	0.964034	0.8636	0.772086
60	0.859733	0.8182	0.681011
75	0.847103	0.7727	0.596384
90	0.669325	0.7273	0.518087
120	0.420314	0.6364	0.379992
150	0.394292	0.5455	0.265678
210	0.365858	0.3636	0.103647
270	0.126156	0.1818	0.020735
0	1	0.954545	0.974029
15	0.81958	0.886364	0.820077
30	0.682517	0.818182	0.681011
45	0.565035	0.75	0.556452
60	0.359441	0.681818	0.445999
75	0.218182	0.613636	0.349227
90	0.157063	0.545455	0.265678
120	0.107133	0.409091	0.136242
150	0.086713	0.272727	0.053151
0	1	1	1.085111
15	0.892598	0.944444	0.950268
30	0.811007	0.888889	0.825511
45	0.657814	0.833333	0.710647
60	0.535426	0.777778	0.605472
75	0.284822	0.722222	0.509773
90	0.248439	0.666667	0.423327
120	0.135459	0.555556	0.27724
150	0.090001	0.444444	0.16515
210	0.020231	0.222222	0.03304

After determining the $\theta_{predicted}$ and θ_{expt}, error minimization between $\theta_{predicted}$ and θ_{expt} was conducted to obtain the accurate values of kinetic parameter k_θ and order of the reaction n which are shown in the following Table 13:

Table 13: Kinetic parameter and order of the reaction kinetics

Kinetic parameter (k_θ)	Order of the reaction (n)
-2.40455 (1/time)	0.56923

After completing these, a graphical comparison between the experimental θ (θ_{expt}) and predicted θ ($\theta_{predicted}$) was carried out by plotting the values of $\theta_{predicted}$ and θ_{expt} against the dimensionless Γ (Fig. 21). As can be seen from Fig. 21 that the experimental results of kinetic pattern of adsorption of organoclay in oil water emulsion follow the dimensionless kinetic model very closely. Therefore, it can be concluded that the dimensionless kinetic model is a good representation of actual kinetic behavior of adsorption of organoclay in oil water emulsion.

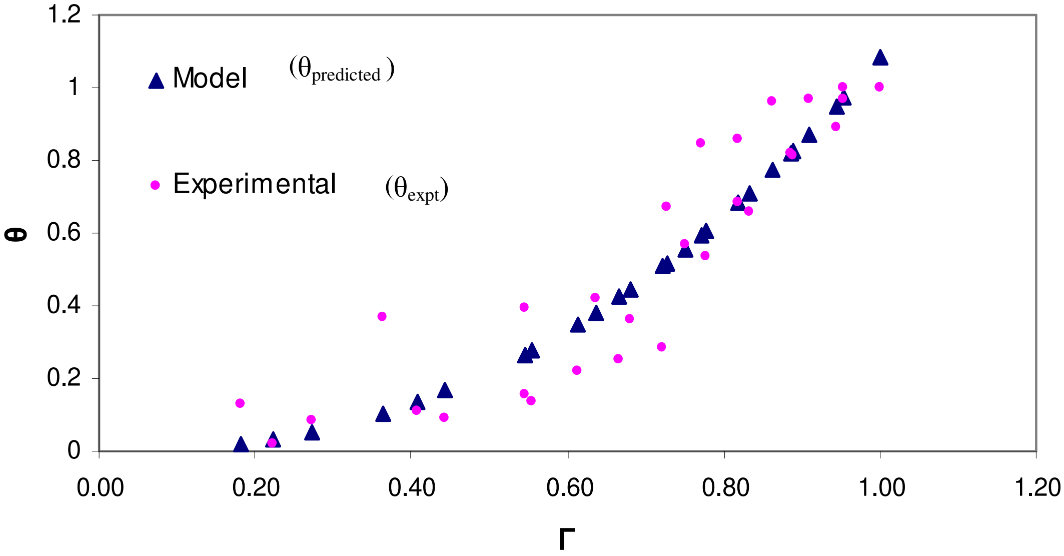


Fig. 21- Graphical representation of experimental and dimensionless kinetic model for 750, 1000 and 1500 ppm oil-water emulsion

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The following conclusions were reached as a result of this research project:

1. The organoclay PS-12385 can be applied to effectively remove SAE 30 Motor Oil from oil -water emulsions.
2. Batch kinetic studies confirmed that equilibrium time can be reached within 3hrs of contact between organoclay and oil- water emulsion, depending on the concentration of the particular oil-water to be treated.
3. The percentage of oil removal from SAE 30 oil-water emulsion in organoclay media is not a fixed value and varies depending on the concentration of the oil water emulsion. From this particular study, the percentages of oil removal were found to be 28.20% for 750ppm emulsion, 35.75% 1000 ppm emulsion and 40.036% for 1500 ppm emulsion. So it can be concluded that the removal capacity of organoclay is proportional to the concentration of the emulsion.
4. Under similar conditions, organoclay shows reduced oil removal performance in case of higher concentration oil- water emulsions (concentration beyond 1500 ppm). This behavior of organoclay can be attributed to the fact that it is not possible to make homogeneous emulsions, which is a basic requirement of measuring adsorption capacity of organoclay, using the similar conditions as the

ones used for emulsions within 1500 rpm. Therefore a different set of conditions should be applied for preparing emulsions beyond 1500 ppm and then measure the adsorption capacity of organoclay.

5. The Freundlich isotherm model can effectively provide the amount of organoclay required to lower the oil in the oil-water emulsion to a desired level.
6. The kinetic behavior of organoclay in SAE 30 motor oil-water emulsion was compared with those proposed and established by first order kinetic model of Vermuelen and Heister.[31] Although for the most part the experimental results seem to match the model data, for some part, the experimental results, i.e., the kinetic behavior of organoclay in SAE 30 oil water emulsion, deviated a little from the model data and this phenomenon was evident from the comparison of the experimental and model data. The author believes that the reason behind this discrepancy was due to the kinetic behavior of the organoclay that was used in the experiment. It is to be noted here that the Vermulen and Heister model follows first order kinetics. Therefore, if the experimental data were to match the model data, the organoclay must follow the first order kinetic all through. However, as mentioned before, although experimental data matched the model data for a large portion, it failed to match totally with the model data. In this connection, the author's speculation is that probably the organoclay in the experiment did not follow first order kinetics completely thereby resulting in a discrepancy between the experimental and model data.

7. To establish a model that matches the kinetic behavior of organoclay in SAE 30 oil water emulsion, a dimensionless kinetic model was developed. In this model, a dimensionless concentration parameter θ and a dimensionless time parameter Γ were introduced and using least square analysis reaction kinetic parameter and order of reaction were obtained to attain a relationship between experimental and model values of dimensionless concentration parameter. This model matched the experimental results, i.e., the kinetic behavior of organoclay in SAE 30 oil water emulsion pretty closely. Therefore, it can be concluded that this dimensionless model is a good representation of kinetic behavior of organoclay in SAE 30 oil water emulsion.

7.2 Recommendations for future work

The following recommendations can be made on the basis of the results and conclusions and the extrapolations of the work to oil field applications:

1. In this research project a special type of cotton cloth was used to make pouches that contained organoclay. The cotton pouch itself is capable of adsorbing some of the oil. Hence the author wants to recommend further research where organoclay will be put straight into the oil-water emulsion without containing it in any kind of cloth pouches to examine if that arrangement changes the adsorption capacity of the organoclay. Alternative arrangements can be made where metal baskets can be used to contain

organoclay in oil water emulsion so that the materials of the basket do not adsorb any oil.

2. This research project employed SAE 30 motor oil as an adsorbate and organoclay as the adsorbent. Therefore, the results obtained and analyzed in this project represent the adsorption capacity only valid for the system that consists of organoclay and SAE 30 motor oil. A further study can be conducted using other oils with organoclay to verify the adsorption capacity of the organoclay used in this research project.
3. Further study should be conducted to find the efficiency of organoclay in HC removal in combination with GAC. This combination can potentially provide high removal efficiency and excellent reliability in treating contaminated wastewaters.
4. Detailed research on the adsorption capacity of organoclay with actual oil field produced water is required to verify the actual performance of organoclay in removing oil from actual produced water from oil fields.
5. Thorough research work should be done to find the environmental impact of used organoclay during the disposal.

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APPENDIX

Development of kinetic pattern of the organoclay using the adsorption parameters

From Fig. 8, which was obtained from Freundlich Isotherm, adsorption parameters K_f and n were obtained and their values are given below,

Adsorption parameter, $K_f = 1.514(\text{gm/gm})\ (\text{L/gm})^{1/n}$ and

$n = 11.31$.

This model was developed for 1000 ppm oil water emulsion and therefore the value of the amount of organoclay used (m) was 6.0 gm. For this model, total time considered was 99 minutes with an interval of 3 minutes for each step. Following MATLAB coding was developed to examine the kinetic behavior or pattern of the organoclay.

```
Kf min =1.514;
Kf_max =1.514;
n_min =11.31;
n_max =11.31;
m = 6;
t =[0:3:99];
c(1)=3;
qq =1;
tolerance = 0.001;
prime = 0.00001
initial_value = 3;
for K = Kf_min:0.1: Kf_max
    K
    for N =n_min:0.1:n_max
        N
        for i=1:size(t,2)-1
            c(i+1) =
newtonrhapson(c(i),K,m,N,c(i),prime,tolerance);
        end
```

```
        figure(qq)
        plot(t,c ,'r-')
        hold on
        xlabel('Time');
        ylabel('Concentration');

        grid on
    end
    qq = qq + 1;
end
```

Newton-Rhapson method to solve the iteration

```
Function a =
newtonrhapson(c,Kf,m,n,initial_value,prime,tolerance)

x1 = initial_value;
x2 = 10000;
num_iteration = 0;
while abs(x2-x1) > tolerance
    x2 = x1;
    % evaluate f
    f = - x1 + c - Kf * (x1^(1/n)) * m;
    % evaluate f'
    f1 = -(x1-prime) + c - Kf * ((x1-prime)^(1/n)) * m;
    f2 = -(x1+prime) + c - Kf * ((x1+prime)^(1/n)) * m;
    fprime = (f2 - f1) / (2*prime);
    % evaluate new x
    x1 = x1 - (f / fprime);
    num_iteration = num_iteration + 1;
    if num_iteration > 5000;
        abs(x2-x1)
        break;
    end
end
num_iteration
a = x1;
```

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